ニッケル、パラジウムを触媒として用いる
新規炭素－炭素結合切断、形成反応の開発

Novel C-C Bond Cleavage and C-C Bond Formation Reactions
Utilizing Nickel and Palladium as the Catalyst

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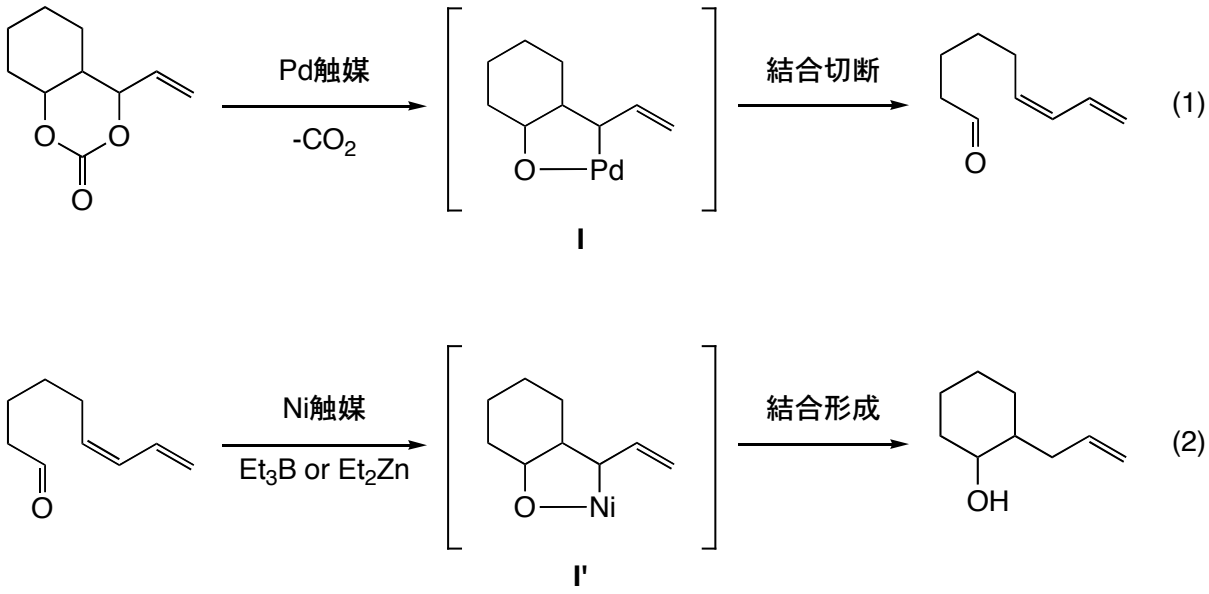
序論

オキサメタラサイクルを中間体とする炭素－炭素結合形成反応が数多く開発されている。その多くは、チタンやジルコニウムなどの前周期遷移金属に関する内容であり、専ら量論的な反応である。[1],[2],[3] かつて、私が所属する研究室では、４－ビニル環状カーボネートがパラジウムの触媒作用により、オキサパラダサイクル **I** を経由し、β-decarbopalladation という全く新しい形式の炭素－炭素結合切断反応を受け、ω－ジエニルアルデヒドを与えることを発見した（式１）。[4] パラジウムのような後周期遷移金属が、酸素との結合能が低いにも拘らず、オキサパラダサイクル **I** を形成し、しかも、対照的な炭素－炭素結合切断反応が触媒的に進行することは、斬新であるばかりではなく、有機合成化学において、後周期遷移金属のオキサメタラサイクルを活用する反応に飛躍的な進展をもたらした。また、当研究室では、ニッケル触媒、トリエチルホウ素、あるいはジエチル亜鉛共存下、１，３－ジエンとアルデヒドを反応すると、ニッケルの触媒作用により、オキサニッケラサイクル **I'**を経由し、トリエチルホウ素、またはジエチル亜鉛による還元を受け、ビスホモアリルアルコールを与える還元的カップリング反応（ホモアリル化反応）を開発している（式２）。[5] この反応は、形式的に式１の逆反応にあたる。中心金属はいずれも同族の遷移金属でありながら、パラジウムは炭素－炭素結合切断反応に、ニッケルは求核的な炭素－炭素結合形成反応に利用される点で注目に値する。



有機亜鉛や有機ホウ素は Lewis 酸としての性質とニッケルやパラジウムのような遷移金属を低原子価状態に還元する能力を併せ持つ。本論文では、有機亜鉛や有機ホウ素の特異的な反応性をニッケルやパラジウムのような後周期遷移金属のオキサメタラサイクルの反応に活用した効率的な炭素－炭素結合切断反応及び形成反応について四章にわたり論じる。

第１章では、ニッケル触媒を用いる４－ビニル環状カーボネートの炭素－炭素結合切断反応について、第２章では、パラジウム触媒、有機ホウ素を用いる４－ペンテン－１，３－ジオール誘導体の炭素－炭素結合切断反応について、第３章では、ニッケル触媒、有機亜鉛、１，ω－ジエンイン、カルボニル化合物の四成分連結反応について、第４章では、ニッケル触媒、有機亜鉛、１，ω－ジエンイン、アルデヒド、アミンの多成分連結反応について紹介する。

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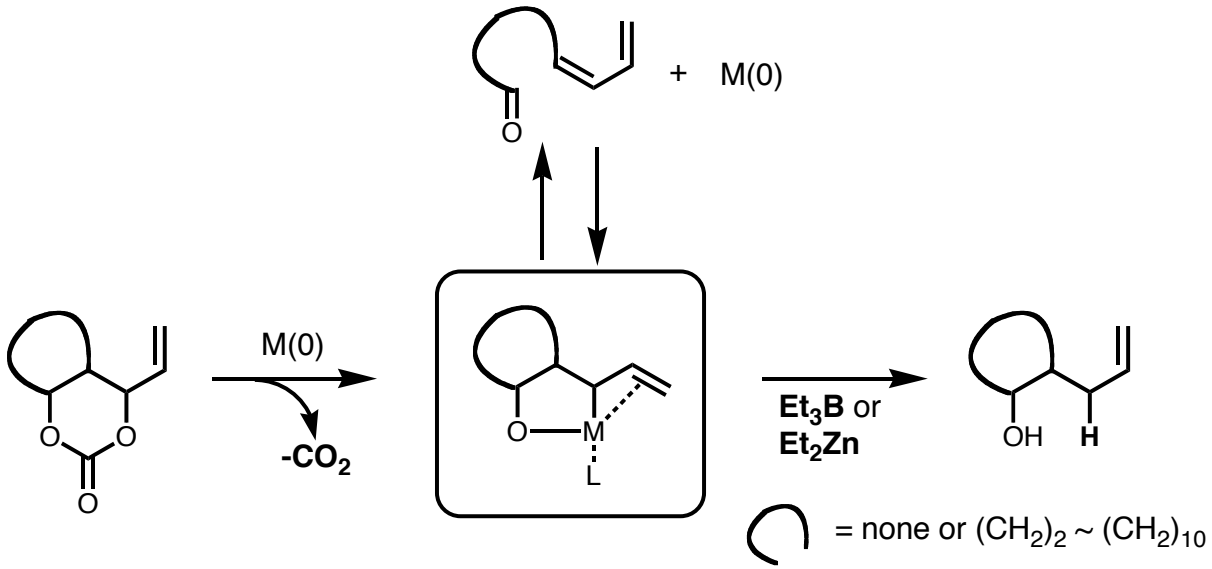
第１章

ニッケル触媒を用いる４－ビニル環状カーボネートの炭素－炭素結合切断反応の開発

１．緒言

近年、遷移金属触媒を用いる有用な炭素－炭素結合切断反応が数多く開発されている。[1],[2]　当研究室では、パラジウム触媒存在下、４－ビニル環状カーボネートを反応させると、炭素－炭素結合切断反応が進行し、ω－ジエニルアルデヒドを高収率で与えることを報告した（Scheme 1）。[3]　反応は常圧、室温で進行し、オキサパラダシクロペンタンのβ-decarbopalladation というこれまでにはない新形式の炭素－炭素結合切断反応である。本反応は、反応機構の観点から興味深いだけでなく、生成物のω－ジエニルアルデヒドは、分子内に１，３－ジエン、アルデヒドを有する化合物であり、合成反応中間体として有用である。ニッケル触媒、トリエチルホウ素[4]、またはジエチル亜鉛[5]共存下、ω－ジエニルアルデヒドを反応させると、１，３－ジエンとアルデヒドの還元的カップリング反応（ホモアリル化反応）が進行し、ビスホモアリルアルコールを高収率で与える（Scheme 1）。[6]　反応は Ni(0)の１，３－ジエンとアルデヒドに対する酸化的環化付加、トリエチルホウ素、またはジエチル亜鉛によるオキサニッケラシクロペンタン中間体の還元で説明される。ニッケル触媒を用いるホモアリル化反応は、形式的にパラジウム触媒を用いる炭素－炭素結合切断反応の逆反応に相当する。中心金属はいずれも同族の遷移金属でありながら、パラジウムは炭素－炭素結合切断反応に、ニッケルは求核的な炭素－炭素結合形成反応に利用されている点で注目に値する。さらに、重要な知見として、生越、黒澤ら（大阪大学）は、ビス（１，５－シクロオクタジエン）ニッケル（０）、単座のホスフィン配位子、１，３－ジエン、アルデヒドの量論反応により、オキサニッケラシクロペンタン中間体の合成並びに単離に成功し、X－線構造解析によりその立体構造を明らかにした。[7]



Scheme 1. Nickel (or Palladium) Catalyzed Fragmentation of Cyclic Carbonate and Cyclization of ω-Dienyl Aldehyde via An Oxametallacycle

これらの知見は、オキサメタラサイクルとω－ジエニルアルデヒド及び M(0) (M(0)= Pd(0), Ni(0))の平衡が遷移金属の種類に大きく影響することを示すものである。ニッケルの場合には、オキサニッケラサイクル形成の方に平衡が傾き、逆にパラジウムの場合には、オキサパラダサイクルのフラグメンテーションによりω－ジエニルアルデヒド及び Pd(0)を生成する方に平衡が傾く。ニッケルとパラジウムが対照的な反応挙動を示す理由として、ニッケルがパラジウムより強い金属－酸素結合を形成することが挙げられる（DH^{o} (Ni-O) = 60.5 kcal/mol、DH^{o} (Pd-O) = 58.9 kcal/mol for *cis*-$(PH_3)_2M(OMe)Me$）。[8]

著者は、DPPF のような bite angle が大きい二座のホスフィン配位子を用いると、ニッケル触媒でも４－ビニル環状カーボネートの炭素－炭素結合切断反応が進行し、ω－ジエニルアルデヒドを与えることを発見した。[9] すなわち、ホスフィン配位子を使い分けることにより、オキサニッケラサイクルが炭素－炭素結合切断反応の中間体としても作用することが明らかになった。興味深いことに、ニッケル触媒の場合、パラジウム触媒よりもω－ジエニルアルデヒドの収率が向上し、さらに、ジエン部位で

高い *E* 選択性を示した。パラジウムは基質の構造によらず反応を促進させるのに対して、[3]　ニッケルの場合には、反応が基質の構造に大きく依存し、適切なホスフィン配位子の選択が必要である。

本章では、ニッケル触媒、ホスフィン配位子を用いる４－ビニル環状カーボネートの炭素－炭素結合切断反応の反応性及び選択性について報告する。

１－１　結果及び考察

常圧窒素雰囲気下、$Ni(cod)_2$ (0.1 mmol)、PPh_3 (0.4 mmol)、４－ビニル環状カーボネート **1** (1 mmol)、溶媒にアセトニトリル (5 ml)を用いて反応を行った。その結果を Table 1 に示す。また、$Pd_2(dba)_3CHCl_3$ を用いた反応の結果も併せて示す。[3a]

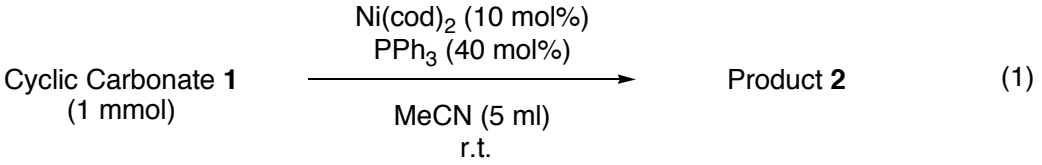
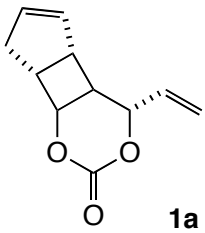
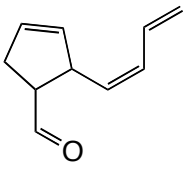
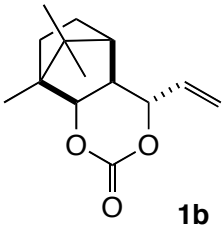
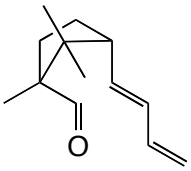
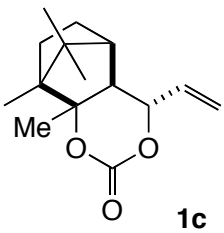
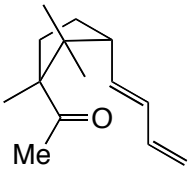
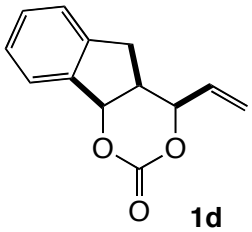
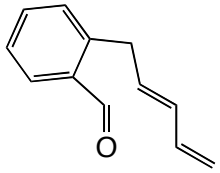
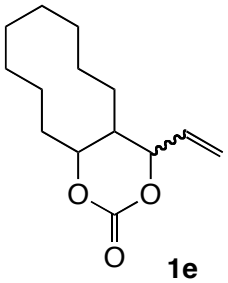
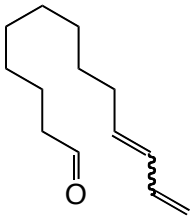
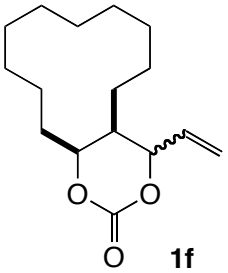
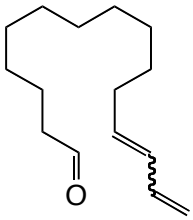
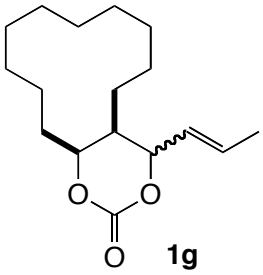
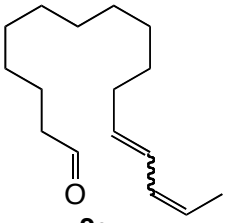


Table 1. Synthesis of ω-Dienyl Aldehyde **2** by Nickel-Catalyzed Decarboxylative Ring-Opening Reaction of Cyclic Carbonate **1**

Run	Cyclic Carbonate **1**	Time (h)	Product **2**	Ni	Pd
				% yield [*E* : *Z*]	% yield [*E* : *Z*]
1	 **1a**	2	 **2a**	75 [1 : 2.4]	65 [1 : 4.4][a]
2	 **1b**	0.5	 **2b**	96 [only *E*]	70 [only *E*][b]
3	 **1c**	24[c]	 **2c**	99 [only *E*]	91 [only *E*][b]

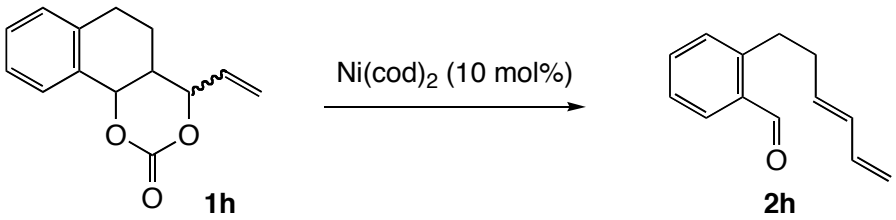
(Table 1, continued.)

4	 **1d**	6	 **2d**	78 [2 : 1]	87 [1.7 : 1][a]
5	 **1e**	24	 **2e**	97 [1 : 1]	91 [1 : 1][a]
6	 **1f**	24	 **2f**	85 [1 : 1]	85 [1 : 3][b]
7	 **1g**	24	 **2g**	98 [1 : 1][d]	78 [1 : 8][a,d]

[a] Yield obtained using $Pd_2(dba)_3$•$CHCl_3$[3a]. [b] Reference 3a. [c] At 50 ºC. [d] *EZ*/*ZE* ratio.

環のひずみが大きい環状カーボネート **1a**-**1d** （Runs 1-4）、tosional strain が大きい環状カーボネート **1e**-**1g** （Runs 5-7）の場合には、室温で速やかに炭素－炭素結合切断反応が進行し、高収率でω－ジエニルアルデヒド **2a**-**2g** を与えた。**1d** は例外的ではあるが、ニッケル触媒を用いた方が、パラジウム触媒よりも生成物の収率が向上した。

ひずみがない六員環カーボネート **1h** の場合、$Ni(cod)_2/PPh_3$ では全く反応は進行しなかった（Table 2, run 1）。パラジウムの場合は対照的であり、室温で速やかに **1h** の炭素－炭素結合切断反応が進行し、高収率かつ *E* 選択的にω－ジエニルアルデヒド **2h** を与える（Table 2, footnote b）。



(2)

Table 2. Effects of Phosphine on the Fragmentation of Cyclic Carbonate **1h**

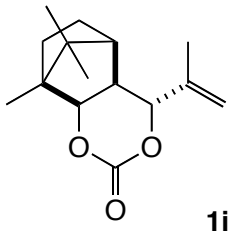
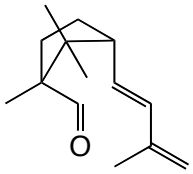
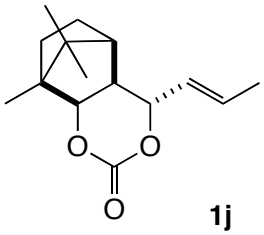
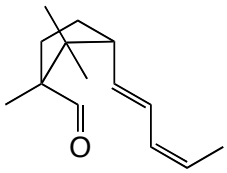
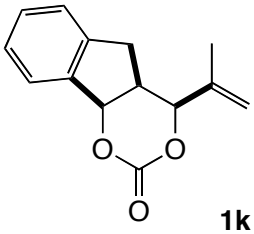
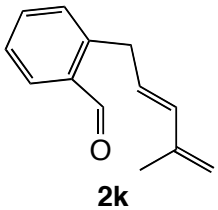
Run	Phosphine / Solvent[c]	Temp. (ºC) / Time (h)	% Yield [*E* : *Z*][d]	Bite angle (º)
1	PPh_3 / MeCN	81 / 24	No Reaction	- - -
2	*n*-Bu_3P / MeCN	81 / 24	No Reaction	- - -
3	Cy_3P / MeCN	81 / 24	No Reaction	- - -
4	DPPE / THF	25 / 48	No Reaction	85
5	DPPP / THF	25 / 48	No Reaction	90-95
6	DPPB / MeCN	25 / 20	76 [20 : 1]	94-99
7	DPPB / THF	25 / 4	76 [> 20 : 1]	94-99
8	DPPF / THF	25 / 4	76 [18 : 1]	99-105
9	DPPF / ether	25 / 2	75 [only *E*]	99-105

[a] Reaction conditions: **1h** (1 mmol), $Ni(cod)_2$ (0.1 mmol), and phosphine (0.4 mmol for a monodentate and 0.2 mmol for a bidentate ligand) in a solvent (5 ml) under N_2.
[b] **2h** in 77% (*E*/*Z* = 10 : 1) using $Pd_2(dba)_3$•$CHCl_3$ as a catalyst.[3a]
[c] MeCN = acetonitrile, THF = tetrahydrofuran, Cy = cyclohexyl,
DPPE = 1,2-bis(diphenylphosphino)ethane, DPPP = 1,3-bis(diphenylphosphino)propane,
DPPB = 1,4-bis(diphenylphosphino)butane, DPPF = 1,1'-bis(diphenylphosphino)ferrocene.
[d] Yields refer to the isolated spectroscopically homogenious **2h**

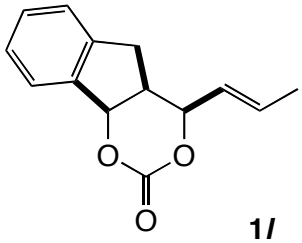
本反応はホスフィン配位子の効果が大きく、単座のトリアルキルホスフィンでは全く反応は進行しなかった（Table 2, Runs 2 and 3）。また、DPPE や DPPP のような二座のホスフィン配位子を用いた場合も、反応は進行しなかった（Table 2 Runs 4 and 5）。同じ二座配位子の中でも、bite angle が大きい DPPB や DPPF を用いた場合、室温で速やかに **1h** の炭素－炭素結合切断反応が進行し、パラジウムの場合よりも、*E* 選択的にω－ジエニルアルデヒドを与えた（Table 2, Runs 6-9）。

種々の４－ビニル環状カーボネートを用いて反応を行った。$Ni(cod)_2$ (0.1 mmol)、PPh_3 (0.4 mmol)、または、 DPPF (0.2 mmol)、４－ビニル環状カーボネート (1 mmol)、各種溶媒 (5 ml)を用いて反応を行った。その結果を Table 3 に示す。

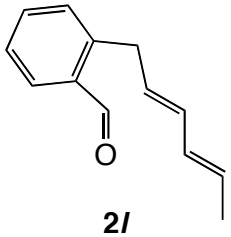
Table 3. Acceleration of the Nickel-Catalyzed Fragmentation of Cyclic Carbonates **1** with Bidentate Phosphine Ligands with Wide Bite Angles[a]

Run	Phosphine/ Solvent[b]	Temp. (°C)/ Time (h)	Ni	Pd
			% yield [*E* : *Z*]	% yield [*E* : *Z*]
	 **1i**		 **2i**	
1	PPh_3 / MeCN	81 / 24	24 [only *E*]	
2	DPPF / ether	25 / 9	98 [only *E*]	55 [only *E*][d]
	 **1j**		 **2j**	
3	PPh_3 / MeCN	50 / 24	NR	
4	DPPF / ether	25 / 9	75 [only *E,Z*]	73 [only *E,Z*][c]
	 **1k**		 **2k**	
5	PPh_3 / MeCN	81 / 24	NR	
6	DPPF / THF	25 / 45	91 [only *E*]	82 [only *E*][c]

(Table 3, continued.)

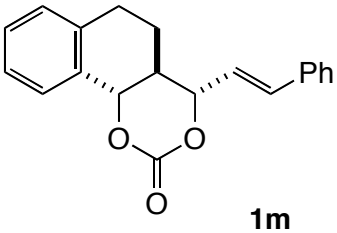


1*l*

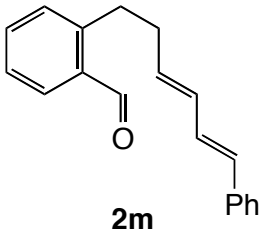


2*l*

7	PPh_3 / MeCN	81 / 24	NR
8	DPPF / ether	25 / 3	81 [only *E,E*]　93 [only *E,E*][c]

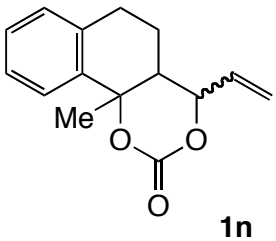


1m

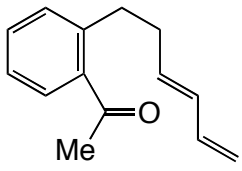


2m

9	PPh_3 / MeCN	81 / 24	NR
10	DPPF / toluene	25 / 10	76 [only *E,E*]　38 [3-isomers][d]



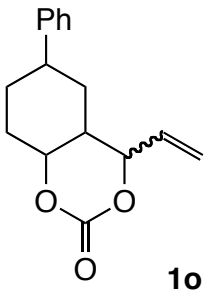
1n



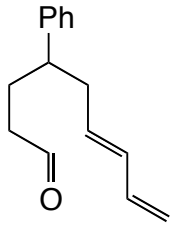
2n

11	PPh_3 / MeCN	50 / 24	44 [1 : 1]
12	DPPF / THF	25 / 21	96 [10 : 1]　81 [1 : 1][c]

(Table 3, continued.)

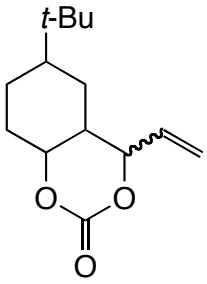


1o

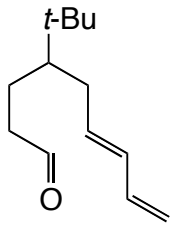


2o

13	PPh_3 / MeCN	81 / 24	NR	
14	DPPF / THF	25 / 4	84 [3 : 1]	42 [2 : 1][d]

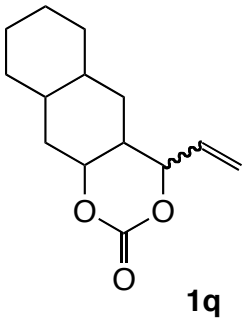


1p

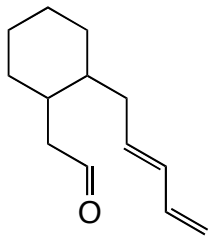


2p

15	PPh_3 / MeCN	81 / 24	NR	
16	DPPF / THF	25 / 9	63 [2 : 1]	20 [4.4 : 1][d]



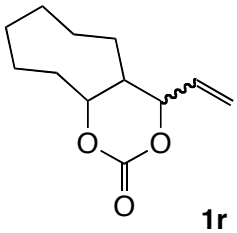
1q



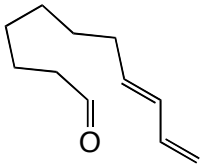
2q

17	PPh_3 / MeCN	81 / 30	NR	
18	DPPF / THF	25 / 2	91 [2 : 1]	54 [1 : 4][d]

(Table 3, continued.)

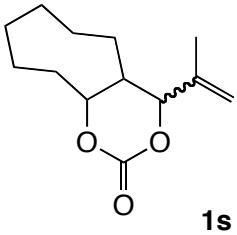


1r

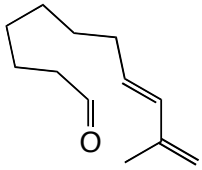


2r

19	PPh_3 / MeCN	81 / 15	40 [1 : 5]	
20	DPPF / ether	25 / 2	94 [2 : 1]	54 [1 : 4][c]

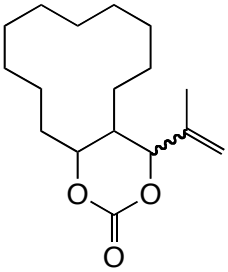


1s

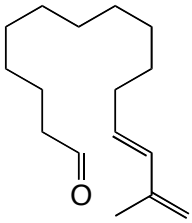


2s

21	PPh_3 / MeCN	81 / 15	NR	
22	DPPF / THF	25 / 24	57 [10 : 1]	10 [1 : 4][d]



1t



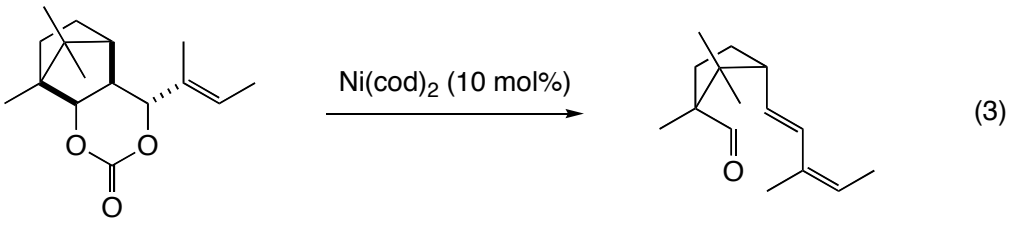
2t

23	PPh_3 / MeCN	81 / 40	NR	
24	DPPF / THF	25 / 72	43 [only *E*]	
25	DPPPent / THF	25 / 24	100 [only *E*]	63 [only *E*][c]

[a] Reaction conditions: **1** (1 mmol), $Ni(cod)_2$ (0.1 mmol), and a phosphine (0.4 mmol for a monodentate and 0.2 mmol for a bidentate ligand) in a solvent (5 ml) under N_2.
[b] DPPPent = 1,5-bis(diphenylphosphino)pentane.
[c] Reference 3a. [d] Yield obtained using $Pd_2(dba)_3$•$CHCl_3$.[3a]
[e] 59% conversion (59% isolated yield based on conversion).

環状カーボネート **1i-1*l*** は環のひずみが大きいにも拘らず、$Ni(cod)_2/PPh_3$ では、ほとんど反応が進行しなかった（Runs 1,3,5 and 7）。ところが、$Ni(cod)_2$/DPPF では、ビニル基の置換様式に拘らず反応が進行し、高収率でω－ジエニルアルデヒド **2i**-**2*l*** を与えた（Runs 2,4,6 and 8）。**1b**、**1d** が $Ni(cod)_2/PPh_3$ で速やかに反応することから（Table 1, Runs 2 and 4）、ビニル基の C1’及び C2’炭素の置換基は反応を阻害することが考えられる。シクロヘキサン誘導体 **1m**-**1q** もホスフィン配位子に DPPF を用いると速やかに反応が進行し、パラジウム触媒よりも飛躍的に収率が向上した（Table 3, Runs 10,12,14,16 and 18）。ばらつきは見られるが、基質によっては高い *E* 選択性を示した（Runs 10 and 12）。Torsional strain が大きい **1r**、**1s** は、パラジウム触媒を用いた場合、低収率かつ *Z* 選択的にω－ジエニルアルデヒド **2r**、**2s** を与える。$Ni(cod)_2/PPh_3$ では、収率、選択性に殆ど変化は見られなかったが（Runs 19 and 21）、DPPF を用いると速やかに反応が進行し、パラジウム触媒よりも良好な収率で **2r**、**2s** を与えた。さらに、*E*、*Z* の立体選択性の逆転が見られたことは注目に値する（Run 20 and 22）。１２員環カーボネート **1t** は、$Ni(cod)_2/PPh_3$ では全く反応せず（Run 23）、DPPF を用いても低収率で **2t** を与える結果となった（Run 24）。イソプロペニル基と１２員環との立体反発により反応が阻害されていることが予想される。ところが、二座のホスフィン配位子である DPPPent[10]を用いると定量的に **2t** を与えた（Run 25）。

触媒量の $Ni(cod)_2$、各種ホスフィンを用いて、ビニル基の C1'と C2'炭素両方に置換基を持つ４－ビニル環状カーボネート **1u** の反応を行った。その結果を Table 4 に示す。



1u　　**2u**　　(3)

Table 4. Effects of Phosphine on the Fragmentation of Cyclic Carbonate **1u**

Run	Phosphine / Solvent[c]	Temp. (°C) / Time (h)	% Yield [*E* : *Z*][d]	Bite angle (°)
1	PPh_3 / MeCN	50 / 24	No Reaction	- - -
2	DPPB / MeCN	50 / 24	35 [almost *E,Z*]	94-99
3	DTPB / MeCN	50 / 24	69 [almost *E,Z*]	> 94-99
4	DPPF / THF	50 / 24	23 [almost *E,Z*]	99-105
5	DTPF / THF	25 / 72	75 [almost *E,Z*]	> 99-105
6	XantPhos / THF	50 / 24	No Reaction	97-133
7	DPEPhos / THF	50 / 24	trace	86-120
8	*rac*-DIOP / THF	50 / 24	37 [almost *E,Z*]	90-120
9	*rac*-DIOP / Toluene	65 / 24	84 [almost *E,Z*]	90-120

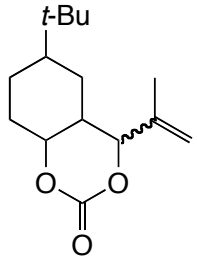
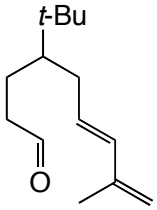
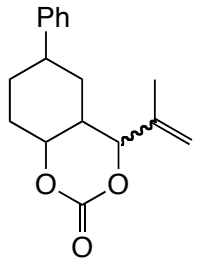
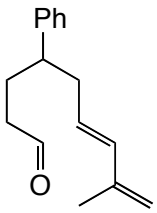
[a] Reaction conditions: **1u** (1 mmol), $Ni(cod)_2$ (0.1 mmol), and phosphine (0.4 mmol for a monodentate and 0.2 mmol for a bidentate ligand) in a solvent (5 ml) under N_2.
[b] **2u** in 58% (only *E,Z*) using $Pd_2(dba)_3$•$CHCl_3$ as a catalyst.[3a]
[c] MeCN = acetonitrile, THF = tetrahydrofuran. DTPB = 1,4-bis[di(*o*-tolyl)phosphino]butane, DTPF = 1,1'-bis[di(*o*-tolyl)phosphino]ferrocene, XantPhos = 4,5-bis(diphenylphosphino)-9,9-dimethylxanthene, DPEPhos = (oxydi-2,1-phenylene)bis(diphenylphosphine), *rac*-DIOP = 1,4-bis(diphenylphosphino)-2,3-*O*-isopropylidene-2,3-butanediol.
[d] Yields refer to the isolated spectroscopically homogenious **2u**.

ホスフィン配位子に PPh_3 を用いて反応させたが、反応は全く進行しなかった（Run

1）。Table 3 に示すように、ビニル基が置換した基質に有効な DPPB や DPPF を用いた場合、低収率ながら立体選択的にω－ジエニルアルデヒド **2u** を与えた（Runs 2 and 4）。DPPB や DPPF と bite angle が等しく、立体的に嵩高い DTPB[11]や DTPF[11]を用いると、良好な収率で **2u** を与えた。DTPF の場合には、長時間を要したが、室温で反応が進行した（Runs 3 and 5）。Bite angle がさらに大きい Xantphos や DPEphos の場合には、ほとんど反応は進行しなかった（Runs 6 and 7）。二座のホスフィン配位子に *rac*-DIOP、溶媒に THF を用いた場合、低収率で **2u** を与えた（Run 8）。ところが、溶媒にトルエンを用いると、立体選択的に高収率で **2u** を与えた（Runs 9）。

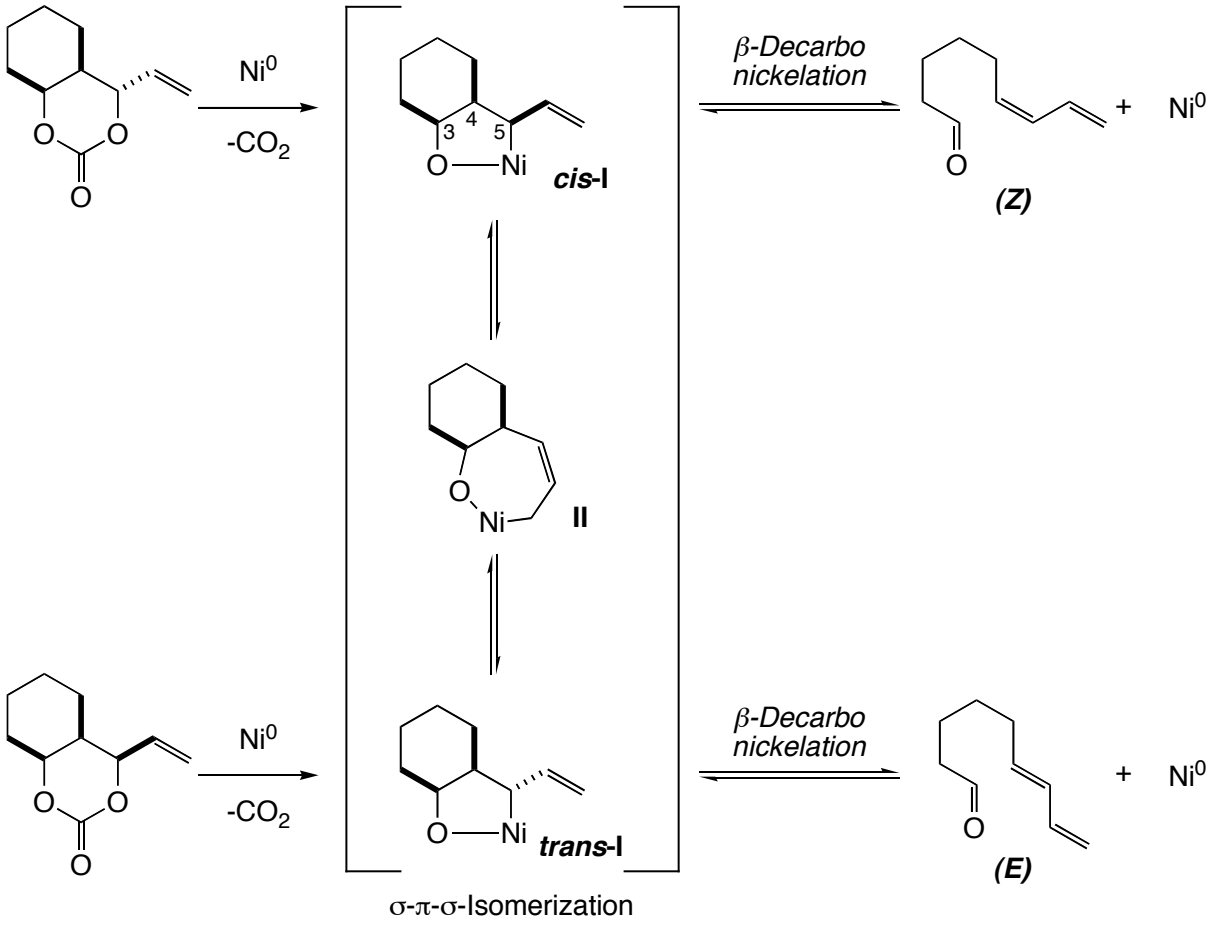
イソプロペニル基が置換した六員環カーボネート **1v**、**1w** は極めて反応性に乏しく、ホスフィン配位子に DPPF を用いても反応は進行しない（Table 5, Runs 1 and 4）。 ホスフィン配位子に *rac*-DIOP、溶媒に THF を用いたが、ほとんど反応は進行しなかった（Table 5, Runs 2 and 5）。トルエン還流下で反応を行うと、低収率ではあるが *E* 体のω－ジエニルアルデヒド **2v**、**2w** が得られた（Table 5, Runs 3 and 6）。

Table 5. Nickel-Catalyzed Decarboxylative C-C Bond Cleavage Reaction of Cyclic Carbonate **1v** and **1w** with DPPF and *rac*-DIOP[a]

Run	Cyclic Carbonate **1**	Phosphine/ Solvent	Temp. (ºC)/ Time (h)	Product **2**	% yield [*E* : *Z*]
1	 **1v**	DPPF/ THF	25 / 48	 **2v**	No reaction
2		*rac*-DIOP/ THF	50 / 24		trace
3		*rac*-DIOP/ Toluene	110 / 24		52 [only *E*]
4	 **1w**	DPPF/ THF	25 / 48	 **2w**	No reaction
5		*rac*-DIOP/ THF	50 / 24		trace
6		*rac*-DIOP/ Toluene	110 / 24		33 [only *E*]

[a] Reaction conditions: **1v** or **1w** (1 mmol), $Ni(cod)_2$ (0.1 mmol), DPPF or *rac*-DIOP (0.2 mmol) in a solvent under N_2.

炭素－炭素結合切断反応におけるω－ジエニルアルデヒドの立体選択性から判断して、次のような反応機構を推定した（Scheme 2）。

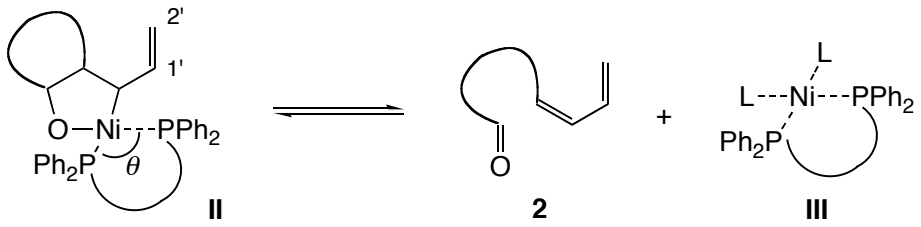


Scheme 2. Plausible Reaction Mechanism for the Nickel-Catalyzed Decarboxylative C-C Bond Cleavage Reaction

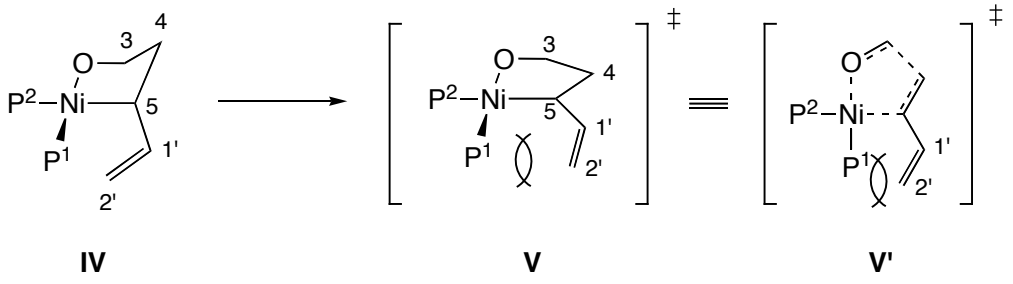
４－ビニル環状カーボネートの C4、C5 位炭素の置換基がトランスの関係にあるカーボネートを例に説明する。Ni(0)のアリル C－O 結合への酸化的付加が立体反転で進行し、脱炭酸を伴い、オキサニッケラシクロペンタン中間体 *cis*-**I** を形成する。*cis*-**I** から直接β-decarbonickelation による C３－C４結合の切断と同時に Ni(0)が再生すると、*Z* 体のω－ジエニルアルデヒドを与える。再生した Ni(0)は新しい触媒サイクルに利用される。もう一つのルートとして、*cis*-**I** の C5 位のビニル基と環との立体反発を避けるように、σ－π－σ異性化が起こり、熱力学的により安定な *trans*-**I** に変換し、β-

decarbonickelation が進行すると、*E* 体のω－ジエニルアルデヒドを与える。

DPPF の bite angle（99-105°）は Ni(0)の正四面体型の配位に丁度一致するため、DPPF の配位により Ni(0)錯体 **III** は安定化すると考えられる。また、オキサニッケラシクロペンタンの Ni(II)の周りの配位は平面四角形型であり、DPPF の bite angle との差が大きいため、DPPF の配位によりオキサニッケラシクロペンタン **II** は大きくひずみ、不安定化すると考えられる。[12] このため、DPPF により **II** のフラグメンテーションが促進され、ω－ジエニルアルデヒド及び **III** に平衡が傾くと考えられる（Scheme 3）。DPPF が配位した Ni(0)錯体 **III** は反応性に富み、アリルカーボネートの C－O 結合に酸化的付加し **II** を形成する。このようにして、触媒サイクルが成立すると考えられる。



Scheme 3. Acceleration of β-C Elimination by Bidentate Ligands with Wide Bite Angles (θ)



Scheme 4. Increase in steric repulsion between P1 and vinyl moiety in a transition state **V**, placing all the P1, P2, Ni, C5, C4, C3, and O atoms in the same plane

ビニル基の C1'炭素が置換した基質は、反応時間が長くなる傾向が見られる（Table 3, Runs 6 and 8, 20 and 22）。この原因として、中間体 **IV** が遷移状態 **V** に近づくときに、ビニル基とリン原子 P1 との立体反発が増大するため反応が阻害されると考えら

れる（Scheme 4）。すなわち、Bite angle が大きい二座のホスフィン配位子の役割について、電子的には、Ni(0)錯体 **III** を安定化し、オキサニッケラサイクル **II** を不安定化することでフラグメンテーションを促進すると考えられる。[13]　立体的には、Ni－C5 結合と C3－C4 結合が共平面を形成することを妨げるため、反応を阻害すると考えられる。

パラジウム触媒のみならず、10 族遷移金属で最も安価なニッケル触媒も PPh_3 および DPPF を用いることにより、様々な構造の４－ビニル環状カーボネートの炭素－炭素結合切断反応を促進し、ω－ジエニルアルデヒドを与えることを明らかにした。ホスフィン配位子は、オキサニッケラサイクル **I** とω－ジエニルアルデヒド及び Ni(0)錯体の平衡を生成系に傾ける役割を果たしていると考えられる。基質の構造に応じてホスフィン配位子を適切に使い分けることにより、広範な４－ビニル環状カーボネートの炭素－炭素結合切断反応が可能である。興味深いことに、以前報告したパラジウム触媒を用いた反応[3a]より生成物の収率が向上し、高い *E* 選択性を示した。反応条件の温和さ、反応基質の有用性、ω－ジエニルアルデヒドの合成反応中間体としての重要性から、本反応の有機合成的意義は極めて高い。

Experimental Section

Reactions employed oven-dried glassware unless otherwise noted. Thin layer chromatography (TLC) employed glass 0.25 mm silica gel plates with UV indicator (Merck, Silica gel $60F_{254}$). Flash chromatography columns were packed with silica gel (Wakogel-C300) as a slurry in hexane. Gradient flash chromatography was conducted eluting with a continuous gradient from hexane to the indicated solvent. Proton and carbon NMR data were obtained with a JEOL-GX400 with tetramethylsilane as an internal standard. Chemical shift values were given in ppm downfield from the internal standard. Infrared spectra were recorded with a JASCO A-100 FT-IR spectrophotometer. High resolution mass spectra (HRMS) were measured with a JEOL JMS-DX303. Combustion analyses were performed by the Instrumental Analysis Center of Nagasaki University. Analysis agreed with the calculated values within $\pm$ 0.4%.

Solvents and Reagents. Tetrahydrofuran and ether were distilled from a blue solution of sodium benzophenone ketyl under N_2 immediately prior to use. Acetonitrile was distilled under nitrogen from calcium hydride. $Ni(cod)_2$ (Kanto Kagaku Kogyo, Co., Ltd.), triphenylphosphine, tri(*n*-butyl)phosphine, tri(*c*-hexyl)phosphine, 1,2-bis(diphenylphosphino)ethane, 1,3-bis(diphenylphosphino)propane, 1,4-bis(diphenyphosphino)butane, 1,1'-bis(diphenylphosphino)ferrocene, 4,5-bis(diphenylphosphino)-9,9-dimethylxanthene, (oxydi-2,1-phenylene)bis(diphenylphosphine), 1,4-bis(diphenylphosphino)-2,3-*O*-isopropylidene-2,3-butanediol (Aldrich Co., Ltd.) were purchased and used without further purification. Cyclic carbonates **1a** – **1w** were prepared according to the method reported previously from our laboratories.[3],[14],[15] One typical example is shown below.

Preparation of Cyclic Carbonate (**1e**): A 300 mL of three-necked round-bottomed flask, equipped with a dropping funnel, a rubber septum, and an air condenser at the top of which is attached a three-way stopcock fitted a nitrogen balloon, is charged with freshly distilled THF (30 mL) and diisopropylamine (4.6 mL, 33 mmol) via a syringe under nitrogen. Into the flask was added *n*-butyllithium (20 mL, 33 mmol; 1.6 M hexane solution) at -78 ˚C, and the mixture was stirred for 1 hour. To the reaction mixture was added cyclodecanone (4.6 g, 30 mmol) dissolved in THF (10 mL) via a dropping funnel at -78 ˚C, and the mixture was stirred at 0 ˚C for 1 h. A solution of acrolein (2.4 mL, 36 mmol) in dry THF (10 mL) was quickly added at -78 ˚C and stirred for 1 minute. The reaction mixture was quenched by 2M HCl at -78 ˚C and extracted with ethyl acetate (2 x 30 mL). After being washed with sat. $NaHCO_3$ and sat. NaCl, and the combined extracts were dried ($MgSO_4$). The solvent was removed *in vacuo*, and the residue was subjected to column chromatography on silica gel (hexane/ethyl acetate = 8:1, v/v) to give aldol product in 94% yield.

Into a suspension of lithium aluminum hydride (1.5 g, 40 mmol) in ether (30 mL) was added the aldol product (5.7 g, 27 mmol) dissolved in dry ether (10 mL) at 0 ˚C. After being stirred for 30 min at the same temperature, the excess lithium aluminum hydride was decomposed by adding aqueous THF (THF/water = 1:1, v/v) dropwise until gray slurry turned into white granules. After filtration with suction through a celite pad on a glass filter, the filtrate was washed with 15% aqueous NaOH and sat. NaCl, and separated. Organic phase was dried ($MgSO_4$), and the solvent was removed *in vacuo*. The residue was subjected to column chromatography on silica gel (hexane/ethyl acetate = 8:1, v/v) to give diol in 96% yield.

To a solution of the diol (4.23 g, 20 mmol) and triethylamine (24 mL, 170 mmol) in dichloromethane (30 mL) was added methyl chloroformate (11 mL, 140 mmol) at 0 ˚C. The solution was stirred at room temperature for 24 hours, and then 20 mL of water and 2M HCl (15 mL) were added at 0 ˚C, and extracted with dichloromethane (2 x 30 mL). The

combined organic layer was dried ($MgSO_4$) and concentrated *in vacuo*, and the residue was subjected to column chromatography on silica gel (hexane/ethyl acetate = 8:1, v/v) to give cyclic carbonate **1e** (2.57 g) in 54% yield. **(*1S,10S,14S*)-14-Vinyl-11,13-dioxabicyclo[8.4.0]tetradecan-12-one** (**1e**): (a mixture of 4 isomers in 2 : 1 : 1 : 1 ratio): IR (KBr disk) 3740 (w), 2985 (m), 2910 (m), 2870 (m), 2360 (m), 1735 (s), 1170 (w), 1125 (w), 1065 (w), 935 (w), 770 (w), 670 (w), 635 (w) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, a major isomer was assigned) δ 1.30 - 1.55 (m, 13 H), 1.81 - 1.88 (m, 2 H), 1.99 - 2.11 (m, 2 H), 4.49 (ddd, *J* = 3.2, 4.4, 8.3 Hz, 1 H), 4.75 (t, *J* = 4.7 Hz, 1 H), 5.39 (d, *J* = 10.2 Hz, 1 H), 5.40 (d, *J* = 17.6 Hz, 1 H), 5.85 (ddd, *J* = 4.7, 10.2, 17.6 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$, a major isomer was assigned) δ 22.6, 22.7, 23.2, 24.0 24.6, 24.9, 25.5, 27.7, 36.4, 78.5, 82.0, 118.7, 134.7, 148.5; HRMS calcd for $C_{14}H_{22}O_3$: 238.1569. Found *m/z* (relative intensity) 238.1570 (M^+, 2), 239 (100), 165 (62), 152 (38), 151 (81).

(*1S,7S,11S*)-11-Vinyl-8,10-dioxatricyclo[5.4.0.0^{2,6}]-3-undecen-9-one (**1a**): Yields: Aldol, 94 %; LAH reduction, 70 %; Carbonation, 66 %; IR (neat) 3450 (m), 2980 (m), 2840 (m), 1760 (s), 1380 (m), 1200 (s), 1100 (s), 990 (m), 930 (m), 770 (m), 720 (s) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 2.47 (ddd, *J* = 2.2, 4.0, 17.2 Hz, 1 H), 2.57 (dt, *J* = 7.3, 1.8 Hz, 1 H), 2.69 (ddq, *J* = 7.3, 17.2, 2.2 Hz, 1 H), 3.13 - 3.22 (m, 2 H), 4.52 (dd, *J* = 4.0, 7.3 Hz, 1 H; coalescing to d, *J* = 4.0 Hz, by irradiation at 2.57), 4.86 (ddt, *J* = 6.2, 7.3, 1.1 Hz, 1 H; coalescing to d, *J* = 6.2 Hz, by irradiation at 2.57), 5.37 (d, *J* = 10.6 Hz, 1 H), 5.44 (dd, *J* = 1.1, 16.9 Hz, 1 H), 5.77 (dq, *J* = 5.5, 2.2 Hz, 1 H), 5.82 (dq, *J* = 5.5, 2.2 Hz, 1 H), 5.89 (ddd, *J* = 6.2, 10.9, 16.9 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 38.0, 43.1, 44.1, 44.2, 80.4, 81.5, 119.2, 132.6, 132.7, 150.0; HRMS calcd for $C_{11}H_{12}O_3$: 192.0786. Found *m/z* (relative intensity) 192.0782 (M^+, 3), 148 (8), 127 (81), 92 (100), 84 (99).

(*2R,6S,7S*)-1,11,11-Trimethyl-6-Vinyl-3,5-dioxatricyclo[6.2.1.0^{2,7}]undecan-4-one (**1b**)

(CCDC-601331)[16]: Yields: Aldol, Quant.; LAH reduction, Quant.; Carbonation, 60%; mp 72.0 – 73.0 ˚C (hexane); IR (KBr disk) 3460 (m), 3020 (m), 2940 (s), 2910 (s), 2850 (m), 1760 (s), 1370 (s), 1220 (s), 1110 (s), 1070 (s), 990 (s), 930 (s) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.92 (s, 3 H), 1.06 - 1.16 (m, 2 H), 1.07 (s, 3 H), 1.62 (m, 1 H), 1.76 (d, *J* = 4.0 Hz, 1 H), 1.83 (m, 1 H), 2.15 (dd, *J* = 8.1, 11.4 Hz, 1 H), 4.21 (d, *J* = 8.1 Hz, 1 H), 4.83 (dd, *J* = 6.6, 11.4 Hz, 1 H), 5.33 (dt, *J* = 10.3, 1.1 Hz, 1 H), 5.40 (dt, *J* = 17.2, 1.1 Hz, 1 H), 5.88 (ddd, *J* = 6.6, 10.3, 17.2 Hz, 1 H); Anal. calcd for $C_{14}H_{20}O_3$: C, 71.16; H, 8.53. Found: C, 71.17; H, 8.47.

(*2R,6S,7S*)-1,2,11,11-Tetramethyl-6-vinyl-3,5-dioxatricyclo[6.2.1.$0^{2,7}$]-undecan-4-one (1c): Yields: Aldol; Quant.; MeLi, 20 %; Carbonation, Quant.; mp 131.0-132.0 ^oC; IR (KBr disk) 3470 (br m), 2950 (m), 2830 (m), 1750 (s), 1450 (w), 1330 (m), 1250 (s), 1230 (s), 1120 (s), 1050 (s), 990 (m), 960 (m) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.94 (s, 3 H), 1.01 (s, 3 H), 1.08 (m, 1 H), 1.23 (s, 3 H), 1.44 (s, 3 H), 1.45-1.55 (m, 2 H), 1.72 (d, *J* = 4.8 Hz, 1 H), 1.82 (d, *J* = 11.0 Hz, 1 H), 1.87 (m, 1 H), 4.80 (dd, *J* = 6.6, 11.0 Hz, 1 H), 5.29 (dt, *J* = 10.3, 1.1 Hz, 1 H), 5.35 (dt, *J* = 16.9, 1.1 Hz, 1 H), 5.85 (ddd, *J* = 6.6, 10.3, 16.9 Hz, 1 H); NOE for H7 (3.1%) and H6 (0%) by irradiation at Me (C2) and for H7 (3.1%) by irradiation at C*H*=CH_2; HRMS calcd for $C_{15}H_{22}O_3$-CO_2: 206.1671. Found *m/z* (relative intensity) 206.1677 (M^+-CO_2, 8), 191 (64), 163 (78), 150 (100), 135 (67), 123 (61).

(*1S,5R,6S*)-5-Vinyl-benzo[8,9]-2,4-dioxabicyclo[4.3.0]nonane-3-one (**1d**): Yields: Aldol, 85 %; LAH reduction, 89 %; Carbonation, 68 % (benzene-ethyl acetate gradient), a single isomer (45%) was obtained after recrystallization from benzene-hexane; mp 86.0 – 87.0 ˚C (benzene-hexane); IR (KBr disk) 3400 (w), 2970 (w), 2900 (m), 1740 (s), 1590 (w), 1180 (m), 1030 (m), 980 (w), 900 (w), 720 (m) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 2.97 (dd, *J* = 7.7, 15.8 Hz, 1 H), 3.10 (dq, *J* = 2.9, 7.7 Hz, 1 H), 3.18 (dd, *J* = 7.7, 15.8 Hz, 1 H), 5.16 (d, *J* = 7.7

Hz, 1 H), 5.52 (d, *J* = 17.2 Hz, 1 H), 5.86 (ddd, *J* = 1.5, 2.9, 5.1 Hz, 1 H), 5.87 (d, *J* = 7.7 Hz, 1 H), 7.26 (d, *J* = 7.7 Hz, 1 H), 7.28 (t, *J* = 7.7 Hz, 1 H), 7.35 (dt, *J* = 1.5, 7.7 Hz, 1 H), 7.50 (d, *J* = 7.7 Hz, 1 H); Anal. calcd for $C_{13}H_{12}O_3$: C, 72.21; H, 5.59. Found: C, 71.96; H, 5.60.

(*1S,12S,16S*)-16-Vinyl-13,15-dioxabicyclo[10.4.0]hexadecan-14-one (**1f**): Yields: Aldol, Quant.; LAH reduction, 97 %; Carbonation, 20 % (hexane-ethyl acetate gradient), a single isomer (12%) was obtained after recrystallization from benzene-hexane; mp 102.0 – 103.0 ˚C (benzene – hexane); IR (KBr disk) 3450 (m), 2950 (s), 2870 (s), 1740 (s), 1130 (s), 1070 (s), 930 (s) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.30 - 1.55 (m, 18 H), 1.66 (m, 1 H), 1.81 - 1.91 (m, 2 H), 4.49 (ddd, *J* = 2.9, 6.2, 7.3 Hz, 1 H), 4.78 (t, *J* = 5.1 Hz, 1 H), 5.40 (d, *J* = 17.2 Hz, 1 H), 5.41 (d, *J* = 10.6 Hz, 1 H), 5.81 (ddd, *J* = 5.1, 10.6, 17.2 Hz, 1 H); Anal. calcd for $C_{16}H_{26}O_3$: C, 72.14; H, 9.84. Found: C, 72.35; H, 9.88.

(*1S,12S,16S*)-(*E*)-16-(2-Methylvinyl)-13,15-dioxabicyclo[10.4.0]-hexadecan-14-one (1g): Yield: Aldol, Quant.; LAH reduction, Quant.; Carbonation, 33% (hexane-ethyl acetate gradient), a single isomer (20%) was obtained after recrystallization from benzene-hexane; mp 115.0-116.0 ^oC; IR (KBr disk) 3440 (br m), 2950 (s), 2860 (s), 1730 (s), 1470 (s), 1390 (s), 1290 (s), 1210 (s), 1120 (s), 1070 (s), 970 (s), 770 (s) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.30-1.50 (m, 18 H), 1.64 (quint, *J* = 7.0 Hz, 1 H), 1.77 (dd, *J* = 0.7, 6.6 Hz, 1 H), 1.81-1.90 (m, 2 H), 4.49 (dt, *J* = 6.6, 3.3 Hz, 1 H), 4.67 (t, *J* = 6.6 Hz, 1 H), 5.46 (ddq, *J* = 6.6, 15.4, 0.7 Hz, 1 H), 5.84 (ddq, *J* = 0.7, 15.4, 6.6 Hz, 1 H); Anal. calcd for $C_{17}H_{28}O_3$: C, 72.82; H, 10.06. Found: C, 72.78; H, 10.07.

5-Vinyl-benzo[9,10]-2,4-dioxabicyclo[4.4.0]decan-3-one (**1h**): (a mixture of 4 isomers in 4 : 3 : 2 : 1 ratio): Yields: Aldol, 96%; LAH reduction, Quant.; Carbonation, 92%; IR (KBr disk) 3420 (m), 2910 (s), 2860 (m), 1750 (s), 1430 (s), 1350 (s), 1230 (s), 1180 (s), 1140 (s), 1060

(s), 990 (s), 940 (s), 760 (s) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, a major isomer was assigned) δ 1.92 – 2.10 (m, 2 H), 2.38 (dddm, *J* = 5.5, 8.8, 11.4 Hz, 1 H), 2.90 - 2.95 (m, 2 H), 5.10 (br t, *J* = 5.5 Hz, 1 H), 5.32 (d, *J* = 10.6 Hz, 1 H), 5.46 (br d, *J* = 15.0 Hz, 1 H), 5.54 (br d, *J* = 8.8 Hz, 1 H), 5.96 (ddd, *J* = 5.5, 10.6, 15.0 Hz, 1 H), 7.16 (d, *J* = 8.1 Hz, 1 H), 7.25 (t, *J* = 8.1 Hz, 1 H), 7.26 (t, *J* = 8.1 Hz, 1 H), 7.57 (d, *J* = 8.1 Hz, 1 H); Anal. calcd for $C_{14}H_{14}O_3$: C, 73.02; H, 6.13. Found: C, 72.78; H, 5.99.

(*2R,6S,7S*)-6-(1-Methylvinyl)-1,11,11-Trimethyl-3,5-dioxatricyclo[6.2.1.$0^{2,7}$]undeca-4-one (**1i**): Yields: Aldol, Quant.; LAH reduction, 95%; Carbonation, 53% (hexane-ethyl acetate gradient), a single isomer (40%) was obtained after recrystallization from benzene-hexane; mp = 96.0 – 97.0 ˚C (benzene-hexane); IR (KBr disk) 3450 (m), 3025 (w), 2900 (s), 2825 (w), 1740 (s), 1640 (w), 1190 (s), 1090 (s), 1070 (w), 1040 (s), 1000 (m), 940 (m), 880 (m), 780 (w), 760 (w), 720 (m) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.91 (s, 3 H), 1.08 (s, 3 H), 1.10 - 1.19 (m, 2 H), 1.19 (s, 3 H), 1.62 (m, 1 H), 1.80 (m, 1 H), 1.83 (s, 3 H), 1.86 (m, 1 H), 2.24 (dd, *J* = 8.1, 11.4 Hz, 1 H), 4.20 (d, *J* = 8.1 Hz, 1 H), 4.83 (d, *J* = 11.4 Hz, 1 H), 5.30 (d, *J* = 1.1 Hz, 2 H). Anal. calcd for $C_{15}H_{23}O_3$: C, 71.91; H, 8.79; Found: C, 72.02; H, 8.81.

(*2R,6S,7S*)-(*E*)-6-(2-Methylvinyl)-1,11,11-trimethyl-3,5-dioxatricyclo[6.2.1.$0^{2,7}$]-undeca-4-one (1j): Yields: Aldol, 97%; LAH reduction, 85%; Carbonation, 43%, a single isomer (32%) was obtained after recrystallization from hexane; mp 79.0-80.0 ^oC; IR (KBr disk) 3200 (w), 3050 (w), 2950 (s), 2850 (m), 1750 (s), 1650 (w), 1480 (m), 1420 (m), 1350 (m), 1320 (m), 1280 (w), 1200 (s) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.90 (s, 3 H), 1.06 (s, 3 H), 1.08-1.14 (m, 2 H), 1.17 (s, 3 H), 1.62 (m, 1 H), 1.77 (dd, *J* = 1.8, 6.6 Hz, 3 H), 1.79-1.89 (m, 2 H), 2.14 (dd, *J* = 8.1, 11.4 Hz, 1 H), 4.19 (d, *J* = 8.1 Hz, 1 H), 4.77 (dd, *J* = 7.7, 11.4 Hz, 1 H), 5.47 (ddq, *J* = 7.7, 15.4, 1.8 Hz, 1 H), 5.83 (ddd, *J* = 1.8, 6.6, 15.4 Hz, 1 H). Anal. Calcd for $C_{15}H_{23}O_3$: C, 71.97; H, 8.86. Found: C, 71.75; 8.85.

(*1S,5R,6S*)-5-(1-Methylvinyl)-benzo[8,9]-2,4-dioxabicyclo[4.3.0]nonane-3-one (1k): Yields: Aldol, Quant; LAH reduction, Quant; Carbonation, 57% (benzene-ethyl acetate gradient), a single isomer (45%) was obtained after recrystallization from benzene-hexane; mp 99.0 – 100.0 ˚C (benzene – hexane); IR (KBr disk) 2925 (w), 2900 (w), 1740 (s), 1600 (w), 1110 (m), 1080 (m), 1040 (m), 1020 (m), 920 (w), 900 (m), 760 (m) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.85 (t, J = 1.5 Hz, 3 H), 2.87 (dd, J = 7.7, 16.9 Hz, 1 H), 3.11 (dd, J = 7.7, 16.9 Hz, 1 H), 3.21 (dq, J = 2.9, 7.7 Hz, 1 H), 5.02 (d, J = 1.5 Hz, 1 H), 5.11 (dd, J = 1.5, 2.9 Hz, 1 H), 5.29 (d, J = 1.5 Hz, 1 H), 5.88 (d, J = 7.7 Hz, 1 H), 7.25 (d, J = 7.7 Hz, 1 H), 7.28 (t, J = 7.7 Hz, 1 H), 7.35 (dt, J = 1.5, 7.7 Hz, 1 H), 7.50 (d, J = 7.7 Hz, 1 H); Anal. calcd for $C_{14}H_{14}O_3$: C, 72.96; H, 6.08. Found: C, 72.78; H, 6.15.

(*1S,5R,6S*)-(*E*)-5-(2-Methylvinyl)-benzo[8,9]-2,4-dioxabicyclo[4.3.0]nonane-3-one (1*l*): Yields: Aldol, 96%; LAH reduction, Quant.; Carbonation 19% (benzene-ethyl acetate gradient), a single isomer (14%) was obtained after recrystallization from ethyl acetate-hexane; mp 73.0 – 74.0 ˚C (ethyl acetate-hexane); IR (KBr disk) 3420 (m), 3000 (m), 2925 (m), 2850 (m), 1740 (s), 1610 (w), 1220 (s), 1080 (s), 950 (s), 910 (m), 890 (w), 750 (s) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.78 (br d, J = 6.6 Hz, 3 H), 2.99 - 3.10 (m, 2 H), 3.24 (m, 1 H), 5.10 (dm, J = 7.3 Hz, 1 H), 5.55 (ddm, J = 7.3, 15.4 Hz, 1 H), 5.84 (br d, J = 7.3 Hz, 1 H), 5.93 (dq, J = 15.4, 6.6 Hz, 1 H), 7.26 (d, J = 7.3 Hz, 1 H), 7.28 (t, J = 7.3 Hz, 1 H), 7.34 (t, J = 7.3 Hz, 1 H), 7.50 (br d, J = 7.3 Hz, 1 H); Anal. calcd for $C_{14}H_{14}O_3$: C, 72.96; H, 6.08. Found: C, 72.73; H, 6.12.

1-Methyl-5-vinyl-benzo[9,10]-2,4-dioxabicyclo[4.4.0]decan-3-one (1n): Yields: Aldol, 88%; MeLi, 74%, Carbonation, 61%, a complex mixture was obtained (the ratio was not determined); IR (neat) 2970 (m), 2930 (m), 1750 (s), 1490 (m), 1440 (m), 1340 (s), 1290 (s), 1250 (s), 1160 (s), 1120 (s), 1090 (s), 990 (s), 940 (s), 760 (s) cm^{-1}; ^1H NMR (400 MHz,

$CDCl_3$, a major isomer was assigned) δ 1.75 (s, 3 H), 2.02 (m, 1 H), 2.10-2.24 (m, 2 H), 2.78 (dd, *J* = 2.9, 9.2 Hz, 1 H), 2.96 (dd, *J* = 4.4, 9.2 Hz, 1 H), 4.60 (dd, *J* = 7.7, 10.6 Hz, 1 H), 5.42 (d, *J* = 10.6 Hz, 1 H), 5.56 (dt, *J* = 17.2, 1.5 Hz, 1 H), 5.88 (ddd, *J* = 7.7, 10.6, 17.5 Hz, 1 H), 7.10 (d, *J* = 7.7 Hz, 1 H), 7.22-7.30 (m, 2 H), 7.68 (dd, *J* = 1.5, 7.7 Hz, 1 H); HRMS calcd for $C_{15}H_{16}O_3$: 244.1099. Found *m/z* (relative intensity) 244.1100 (M^+, 80), 200 (14), 185 (100), 144 (45), 129 (70).

8-Phenyl-5-vinyl-2,4-dioxabicyclo[4.4.0]nonan-3-one (**1o**): (a mixture of 4 isomers in 8 : 2 : 2 : 1) Yields: Aldol, 70%; LAH reduction, 100%; Carbonation 19%; IR (KBr disk) 3460 (m), 3030 (m), 2940 (m), 2870 (w), 2360 (w), 1735 (s), 1600 (w), 1370 (s), 1200 (s), 1090 (s), 990 (m), 940 (m), 850 (w), 770 (m), 710 (m), 620 (w) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, a major isomer was assigned) *δ* 1.27 (q, *J* = 12.2 Hz, 1 H), 1.58 - 1.71 (m, 2 H), 1.81 (ddd, *J* = 2.9, 10.7, 12.2 Hz, 1 H), 2.00 (dq, *J* = 13.4, 2.3 Hz, 1 H), 2.07 (dq, *J* = 13.4, 2.3 Hz, 1 H), 2.30 (m, 1 H), 2.68 (tt, *J* = 3.4, 12.2 Hz, 1 H), 4.19 (dt, *J* = 4.6, 10.7 Hz, 1 H), 4.56 (dd, *J* = 7.4, 10.7 Hz, 1 H), 5.34 (d, *J* = 10.3 Hz, 1 H), 5.38 (d, *J* = 17.1 Hz, 1 H), 5.77 (ddd, *J* = 7.4, 10.3, 17.1 Hz, 1 H), 7.16 - 7.33 (m, 5 H); ^{13}C NMR (100 MHz, $CDCl_3$, a major isomer was assigned) δ 31.1, 31.2, 33.3, 41.5, 42.6, 79.9, 85.0, 120.5, 126.5, 126.5, 126.6, 128.5, 128.5, 132.8, 144.3, 148.4; HRMS calcd for $C_{16}H_{18}O_3$: 258.1256. Found *m/z* (relative intensity): 258.1255 (M^+, 100), 196 (20), 185 (34), 170 (67).

8-*tert*-Butyl-5-vinyl-2,4-dioxabicyclo[4.4.0]nonan-3-one (1p): Yields: Aldol, Quant.; LAH reduction, 79%; Carbonation, 41%, complex mixture was obtained (the ratio was not determined); IR (neat) 2930 (s), 2850 (s), 1750 (s), 1390 (m), 1360 (m), 1200 (s), 1130 (m), 1090 (m), 980 (m), 920 (m), 750 (s) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, a major isomer was assigned) δ 0.73-0.96 (m, 2 H), 0.87 (s, 9 H), 1.02-1.21 (m, 2 H), 1.48 (m, 1 H), 1.78-1.95 (m, 2 H), 2.21 (m, 1 H), 4.01 (dt, *J* = 4.4, 11.0 Hz, 1 H), 4.50 (dd, *J* = 7.7, 10.6 Hz, 1 H), 5.38 (dt,

J = 10.3, 1.1 Hz, 1 H), 5.77 (ddd, *J* = 7.7, 10.3, 17.2 Hz, 1 H); HRMS calcd for $C_{14}H_{22}O_3$+H: 239.1647. Found *m/z* (relative intensity) 239.1643 (M+H, 10), 194 (6), 182 (44), 165 (18), 137 (42), 120 (100).

7-Vinyl-4,6-dioxatricyclo[8.4.0.0^{3,8}]tetradecane-5-one (**1q**): (a mixture of isomers, the ratio was not determined): Yields: Aldol, 49%; LAH reduction, Quant.; Carbonation, 66% (benzene-ethyl acetate gradient), complex mixture was obtained (the ratio was not determined); IR (KBr disk) 3460 (w), 2930 (s), 2860 (s), 1750 (s), 1450 (m), 1380 (s), 1200 (s), 1100 (s), 990 (m), 940 (m), 760 (m) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, a major isomer was assigned) δ 1.19 - 2.10 (m, 15 H), 4.10 (dm, *J* = 10.6 Hz, 1 H), 4.46 (dd, *J* = 7.3, 10.6 Hz, 1 H), 5.34 (d, *J* = 10.6 Hz, 1 H), 5.38 (d, *J* = 16.9 Hz, 1 H), 5.75 (ddd, *J* = 7.3, 10.6, 16.9 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$, a major isomer was assigned) δ 20.5, 26.3, 26.6, 30.5, 31.1, 31.9, 34.0, 34.9, 36.4, 81.1, 85.5, 120.0, 133.1, 148.6; HRMS calcd for $C_{14}H_{20}O_3$: 237.1491. Found *m/z* (relative intensity) 237.1471 (M^+, 3), 192 (9), 174 (19), 163 (39), 135(100), 121 (26), 107 (24).

12-Vinyl-9,11-dioxabicyclo[6.4.0]dodecan-10-one (**1r**): (a mixture of 4 isomers in 4 : 2 : 1 : 1): Yields: Aldol, Quant.; LAH reduction, 91%; Carbonation, 93%; IR (KBr disk) 2920 (s), 2840 (s), 1750 (s), 1210 (s), 1130 (s), 1090 (s), 990 (s), 930 (s), 760 (s) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, a major isomer was assigned) δ 1.26 - 2.12 (m, 13 H), 4.30 (dm, *J* = 10.6 Hz, 1 H), 4.96 (dm, *J* = 4.4 Hz, 1 H), 5.38 (dt, *J* = 10.3, 1.1 Hz, 1 H), 5.49 (dt, *J* = 17.2, 1.1 Hz, 1 H), 5.87 (ddd, *J* = 4.4, 10.3, 17.2 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$, a mixture of 4 isomers) δ 18.9, 21.3, 21.4, 21.8, 22.4, 24.3, 24.4, 24.9, 25.0, 25.4, 25.9, 26.1, 26.3, 26.9, 27.3, 27.4, 28.7, 28.9, 29.0, 31.4, 31.6, 37.7, 37.8, 39.7, 78.8, 81.0, 81.5, 82.8, 83.6, 83.7, 84.5, 118.1, 118.4, 120.2, 121.1, 131.0, 132.5, 133.4, 134.5, 148.6, 148.8, 149.3; HRMS calcd for $C_{12}H_{18}O_3$: 211.1334. Found *m/z* (relative intensity) 211.1324 (M^+, 55), 138 (65), 137 (100), 123 (81)

16-(1-Methylvinyl)-13,15-dioxabicyclo[10.4.0]hexadodecan-14-one (**1t**): (a mixture of 3 isomers in 2 : 2 : 1): Yields: Aldol, Quant.; LAH reduction, 81%; Carbonation, 40% (hexane-ethyl acetate gradient), a single isomer (34%) was obtained after recrystallization from benzene-hexane; mp 119.0 – 120.0 ˚C (benzene-hexane); IR (KBr disk) 3450 (m), 2910 (s), 2830 (s), 1760 (s), 1470 (m), 1380 (m), 1260 (m), 1200 (s), 1120 (s), 900 (m) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, a major isomer was assigned) δ 1.36 - 1.55 (m, 18 H), 1.63 (dq, *J* = 13.9, 7.0 Hz, 1 H), 1.85 (dq, *J* = 13.9, 7.0 Hz, 1 H), 2.01 (dq, *J* = 3.3, 6.2 Hz, 1 H), 4.47 (dt, *J* = 3.3, 7.0 Hz, 1 H), 4.66 (d, *J* = 6.2 Hz, 1 H), 5.06 (s, 1 H), 5.12 (s, 1 H). Anal. calcd for $C_{17}H_{28}O_3$: C, 72.82; H, 10.06. Found: C, 72.76; H, 10.01.

(*2R,6S,7S*)-(*E*)-6-(1,2-Dimethylvinyl)-1,11,11-trimethyl-3,5-dioxatricyclo[6.2.1.$0^{2,7}$]undeca-4-one (1u): Yields: Aldol, 97%; LAH reduction, 98%; Carbonation, 20%, a single isomer was obtained; IR (neat) 3000 (br m), 2900 (w), 2800 (w), 1740 (s), 1640 (w), 1380 (m), 1320 (w), 1220 (m), 1190 (m), 1180 (m), 1100 (m), 1080 (w), 1040 (m), 1000 (m) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.90 (s, 3 H), 1.07 (s, 3 H), 1.08-1.18 (m, 2 H), 1.19 (s, 3 H), 1.08-1.18 (m, 2 H), 1.19 (s, 3 H), 1.57-1.67 (m, 2 H), 1.67 (d, *J* = 6.2 Hz, 3 H), 1.69 (s, 3 H), 1.82 (m, 1 H), 2.26 (dd, *J* = 8.1, 11.4 Hz, 1 H), 2.26 (dd, *J* = 8.1, 11.4 Hz, 1 H), 4.18 (d, *J* = 8.1 Hz, 1 H), 4.76 (d, *J* = 11.4 Hz, 1 H), 5.57 (q, *J* = 6.2, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 10.8, 11.0, 13.3, 29.0, 29.7, 32.8, 46.7, 47.6, 49.5, 85.1, 88.2, 125.8, 131.5, 152.1; HRMS calcd for $C_{16}H_{24}O_3$: 264.1725. Found *m/z* (relative intensity) 264.1715 (M^+, 25), 220 (100), 163 (18), 121 (56).
10.01.

General Procedure for Ni-Catalyzed Decarboxylative Ring-Opening Reaction of Cyclic Carbonate (Table 1, run 5): Into a N_2 purged flask, $Ni(cod)_2$ (14 mg, 0.05 mmol),

triphenylphosphine (52 mg, 0.2 mmol), and cyclic carbonate **1e** (119 mg, 0.5 mmol) were added and dry acetonitrile (2.5 mL) was successively introduced via a syringe. The resulting mixture was stirred at room temperature for 24 hours and was diluted with EtOAc (30 mL) and washed with 2M HCl, sat. $NaHCO_3$, and sat. NaCl. The combined organic phase was dried (MgSO4), and concentrated *in vacuo*. The residue was purified by column chromatography over silica gel (hexane/ethyl acetate = 64:1, v/v) to give dienyl aldehyde **2e** (94 mg) in 97% yield. **10,12-Tridecadienal** (**2e**): IR (neat) 3430 (w), 2930 (s), 2850 (s), 1720 (s), 1700 (m), 1640 (w), 1000 (w), 970 (w), 900 (w), 720 (w), 670 (w), 620 (w) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, *Z*-**2e**) δ 1.24 - 1.42 (m, 10 H), 1.64 (m, 2 H), 2.18 (qm, *J* = 7.8 Hz, 2 H), 2.41 (dt, *J* = 2.0, 7.3 Hz, 2 H), 5.07 (dd, *J* = 2.0, 11.2 Hz, 1 H), 5.17 (dd, *J* = 2.0, 16.8 Hz, 1 H), 5.46 (dt, *J* = 10.5, 7.8 Hz, 1 H), 6.00 (t, *J* = 10.5 Hz, 1 H), 6.63 (dddd, *J* = 16.8, 11.2, 10.5, 1.2 Hz, 1 H), 9.76 (t, *J* = 2.0 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$, *Z*-**2e**) δ 22.1, 29.1, 29.1, 29.1, 29.2, 29.3, 29.5, 43.9, 116.6, 129.0, 132.2, 137.2, 202.6; ^1H NMR (400 MHz, $CDCl_3$, *E*-**2e**) δ 1.24 - 1.42 (m, 10 H), 1.62 (quint, *J* = 7.6 Hz, 2 H), 2.07 (q, *J* = 7.6 Hz, 2 H), 2.41 (dt, *J* = 2.0, 7.6 Hz, 1 H), 4.94 (dm, *J* = 10.3 Hz, 1 H), 5.08 (dm, *J* = 16.7 Hz, 1 H), 5.69 (dt, *J* = 15.0, 7.6 Hz, 1 H), 6.04 (dd, *J* = 10.3, 15.0 Hz, 1 H), 6.30 (dt, *J* = 16.7, 10.3 Hz, 1 H), 9.76 (t, *J* = 2.0 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$, *E*-**2e**) δ 27.7, 29.1, 29.1, 29.1, 29.2, 29.3, 29.5, 32.5, 114.4, 130.8, 132.8, 135.3, 202.6; HRMS calcd for $C_{13}H_{22}O$: 194.1671. Found *m*/*z* (relative intensity): 194.1660 (M^+, 100), 195 (20), 152 (13), 151 (20).

2-(1,3-Butadienyl)-3-cyclopentenecarbaldehyde (**2a**): IR (neat) 3400 (m), 3040 (m), 2990 (m), 2920 (s), 2830 (s), 2740 (s), 1720 (s), 1650 (w), 1620 (w), 1390 (s), 1000 (s), 910 (m), 800 (m), 780 (m), 720 (s) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, *Z*-**2a**) δ 2.44 (ddm, *J* = 10.3, 16.9 Hz, 1 H), 2.84 (ddm, *J* = 6.6, 16.9 Hz, 1 H), 3.24 (ddt, *J* = 2.2, 6.6, 10.3 Hz, 1 H), 4.23 (br t, *J* = 10.3 Hz, 1 H), 5.20 (tm, *J* = 10.3 Hz, 1 H), 5.21 (d, *J* = 10.3 Hz, 1 H), 5.27 (br d, *J* = 16.9 Hz, 1 H), 5.56 (dm, *J* = 5.5 Hz, 1 H), 5.82 (dm, *J* = 5.5 Hz, 1 H), 6.05 (t, *J* = 10.3 Hz, 1

H), 6.72 (dt, *J* = 16.9, 10.3 Hz, 1 H), 9.67 (d, *J* = 2.2 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$, *Z*-**2a**) δ 31.6, 50.4, 53.8, 116.8, 127.0, 131.3, 132.0, 132.5, 136.2, 202.9; ^{1}H NMR (400 MHz, $CDCl_3$, *E*-**2a**) δ 2.63 (dq, *J* = 8.8, 2.2 Hz, 1 H), 2.80 (dm, *J* = 8.8 Hz, 1 H), 3.24 (m, 1 H), 3.82 (tm, *J* = 10.3 Hz, 1 H), 5.04 (br d, *J* = 10.3 Hz, 1 H), 5.16 (br d, *J* = 17.0 Hz, 1 H), 5.30 (dm, *J* = 15.1 Hz, 1 H), 5.63 (dm, *J* = 5.6 Hz, 1 H), 5.73 (dm, *J* = 5.6 Hz, 1 H), 6.15 (dd, *J* = 10.3, 15.1 Hz, 1 H), 6.30 (dt, *J* = 17.0, 10.3 Hz, 1 H), 9.70 (d, *J* = 2.0 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$, *E*-**2a**) δ 32.3, 48.9, 56.5, 116.4, 129.5, 131.0, 131.9, 135.3, 136.4, 201.6; HRMS calcd for $C_{10}H_{12}O$: 148.0880. Found *m/z* (relative intensity) 148.0890 (M^+, 56), 133 (27), 117 (100), 105 (50), 92 (51).

***cis*-1,2,2-Trimethyl-3-[(*1E*)-1,3-butdienyl]cyclopentanecarbaldehyde** (**2b**): IR (neat) 2940 (s), 2860 (m), 2800 (w), 1720 (s), 1650 (w), 1000 (s), 890 (s) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.79 (s, 3 H), 0.96 (s, 3 H), 1.08 (s, 3 H), 1.37 (ddd, *J* = 5.5, 9.2, 13.9 Hz, 1 H), 1.65 (dddd, *J* = 5.5, 9.2, 11.7, 13.9 Hz, 1 H), 1.92 (ddt, *J* = 5.1, 13.9, 9.2 Hz, 1 H), 2.43 (ddd, *J* = 5.1, 11.7, 13.9 Hz, 1 H), 2.50 (q, *J* = 9.2 Hz, 1 H), 4.99 (dd, *J* = 1.5, 10.3 Hz, 1 H), 5.13 (dd, *J* = 1.5, 16.9 Hz, 1 H), 5.57 (dd, *J* = 9.2, 15.4 Hz, 1 H), 6.04 (dd, *J* = 10.3, 15.4 Hz, 1 H), 6.33 (dt, *J* = 16.9, 10.3 Hz, 1 H), 9.64 (s, 1 H); Anal. calcd for $C_{13}H_{20}O$: C, 81.20; H, 10.48. Found: C, 81.39; H, 10.46.

***cis*-1-Acetyl-3-[*(E)*-1,3-butadienyl]-1,2,2-trimethylcyclopentane** (**2c**)**:** IR (neat) 2950 (s), 2860 (m), 1700 (s), 1650 (w), 1600 (w), 1460 (m), 1350 (m), 1230 (m), 1080 (m), 1000 (s) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.67 (s, 3 H), 1.06 (s, 3 H), 1.17 (d, *J* = 0.7 Hz, 3 H), 1.39 (ddd, *J* = 5.1, 9.2, 13.6 Hz, 1 H), 1.57 (dddd *J* = 5.1, 9.2, 11.7, 13.6 Hz, 1 H), 1.83 (ddt, *J* = 5.5, 13.6, 9.2 Hz, 1 H), 2.10 (s, 3 H), 2.48 (q, *J* = 9.2 Hz, 1 H), 2.55 (ddd, *J* = 5.5, 11.7, 13.7 Hz, 1 H), 5.00 (dd, *J* = 1.8, 10.3 Hz, 1 H), 5.10 (dd, *J* = 1.8, 17.2 Hz, 1 H), 5.59 (dd, *J* = 9.2, 15.4 Hz, 1 H), 6.03 (ddd, *J* = 1.8, 10.3, 15.4 Hz, 1 H), 6.33 (dt, *J* = 17.2, 10.3 Hz, 1 H);

HRMS calcd for $C_{14}H_{22}O$: 206.1671. Found *m/z* (relative intensity) 206.1676 (M^+, 100), 191 (14), 122 (18), 83 (70); Anal. Calcd for $C_{14}H_{22}O$: C, 81.50; H, 10.75. Found: C, 81.51; H, 10.83.

***o*-(2,4-Pentadienyl)benzaldehyde** (**2d**): IR (neat) 2950 (w), 2800 (w), 2675 (w), 1700 (s), 1600 (m), 1180 (m), 980 (m), 875 (m), 725 (m) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, *E*-**2d**) δ 3.85 (d, *J* = 6.6 Hz, 1 H), 4.98 (dd, *J* = 1.5, 10.3 Hz, 1 H), 5.07 (dd, *J* = 1.5, 16.5 Hz, 1 H), 5.89 (dt, *J* = 15.0, 6.6 Hz, 1 H), 6.01 (dd, *J* = 10.3, 15.0 Hz, 1 H), 6.30 (dt, *J* = 16.5, 10.3 Hz, 1 H), 7.29 (d, *J* = 7.7 Hz, 1 H), 7.40 (dt, *J* = 1.5, 7.7 Hz, 1 H), 7.53 (dt, *J* = 1.5, 7.7 Hz, 1 H), 7.84 (dd, *J* = 1.5, 7.7 Hz, 1 H), 10.24 (s, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$, *E*-**2d**) δ 35.3, 116.0, 126.8, 130.9, 131.9, 132.4, 132.5, 133.8, 136.5, 142.2, 192.1; ^1H NMR (400 MHz, $CDCl_3$, *Z*-**2d**) δ 4.00 (br d, *J* = 7.7 Hz, 1 H), 5.21 (d, *J* = 10.3 Hz, 1 H), 5.30 (dd, *J* = 1.5, 16.5 Hz, 1 H), 5.57 (dt, *J* = 10.3, 7.7 Hz, 1 H), 6.12 (t, *J* = 10.3 Hz, 1 H), 6.77 (dt, *J* = 16.5, 10.3 Hz, 1 H), 7.32 (d, *J* = 7.7 Hz, 1 H), 7.39 (dt, *J* = 1.5, 7.7 Hz, 1 H), 7.52 (dt, *J* = 1.5, 7.7 Hz, 1 H), 7.82 (dd, *J* = 1.5, 7.7 Hz, 1 H), 10.25 (s, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$, *Z*-**2d**) δ 30.8, 118.4, 126.7, 129.5, 130.1, 130.5, 131.6, 132.3, 133.7, 142.7, 192.3; HRMS calcd for $C_{12}H_{12}O$: 172.0888. Found *m/z* (relative intensity) 172.0871 (M^+, 84), 157 (9), 154 (15), 131 (53), 128 (39), 118 (100).

12,14-Pentadecadienal (**2f**): IR (neat) 2928 (s), 2855 (s), 2361 (m), 2341 (m), 1724 (s), 1679 (s), 1003 (w), 970 (w), 900 (w) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, *E*-**2f**) δ 1.24 - 1.42 (m, 14 H), 1.62 (quint, *J* = 7.3 Hz, 2 H), 2.08 (q, *J* = 7.3 Hz, 2 H), 2.41 (dt, *J* = 1.8, 7.3 Hz, 2 H), 4.94 (d, *J* = 10.2 Hz, 1 H), 5.07 (d, *J* = 16.4 Hz, 1 H), 5.70 (dt, *J* = 14.8, 7.0 Hz, 1 H), 6.04 (dd, *J* = 14.8, 10.2 Hz, 1 H), 6.30 (dt, *J* = 16.4, 10.2 Hz, 1 H), 9.76 (t, *J* = 1.8 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$, *E*-**2f**) δ 27.7, 29.1, 29.3, 29.4, 29.4, 29.5, 29.6, 32.5, 116.6, 129.0, 132.2, 135.4, 202.6; ^1H NMR (400 MHz, $CDCl_3$, *Z*-**2f**) δ 1.24 - 1.42 (m, 14 H), 1.62 (quint, *J* = 7.3 Hz, 2

H), 2.16 (q, *J* = 7.3 Hz, 2 H), 2.41 (dt, *J* = 1.8, 7.3 Hz, 2 H), 5.07 (d, *J* = 10.6 Hz, 1 H), 5.18 (dd, *J* = 1.5, 16.9 Hz, 1 H), 5.44 (dt, *J* = 1.8, 7.3 Hz, 1 H), 5.99 (t, *J* = 10.6 Hz, 1 H), 6.64 (dt, *J* = 16.9, 10.6 Hz, 1 H), 9.76 (t, *J* = 1.8 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$, *Z*-**2f**) δ 22.1, 29.1, 29.3, 29.4, 29.4, 29.5, 29.6, 43.9, 114.4, 130.7, 132.9, 137.2, 202.5; HRMS calcd for $C_{15}H_{26}O$: 222.1984. Found *m/z* (relative intensity): 222.1985 (M^+, 100), 98 (16), 95 (40), 82 (45), 81 (67), 68 (92).

12,14-Hexadecadienal (2g): IR (neat) 3010 (m), 2930 (s), 2860 (s), 2700 (m), 1730 (s), 1460 (m), 1450 (m), 980 (m), 940 (m), 820 (m), 720 (m) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, *Z*,*E*-**2g**) δ 1.20-1.39 (br m, 14 H), 1.63 (quint, *J* = 7.3 Hz, 2 H), 1.77 (dd, *J* = 1.1, 6.6 Hz, 3 H), 2.14 (q, *J* = 7.3 Hz, 2 H), 2.41 (dq, *J* = 1.8, 7.3 Hz, 2 H), 5.29 (dt, *J* = 11.0, 7.3 Hz, 1 H), 5.66 (dq, *J* = 13.6, 6.6 Hz, 1 H), 5.94 (t, J = 11.0 Hz, 1 H), 6.32 (ddq, *J* = 11.0, 13.6, 1.8 Hz, 1 H), 9.76 (t, *J* = 1.8 Hz, 1 H); HRMS calcd for $C_{16}H_{28}O$: 236.2140. Found *m/z* (relative intensity) 236.2136 (M^+, 100), 207 (4), 192 (4), 179 (2), 96 (23), 95 (30).

***o*-(3,5-Hexadienyl)benzaldehyde** (**2h**): IR (neat) 3020 (w), 2910 (w), 2850 (w), 2720 (m), 1700 (s), 1660 (w), 1600 (s), 1010 (s), 900 (m), 750 (s) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, *E*-**2h**) δ 2.39 (q, *J* = 7.7 Hz, 2 H), 3.13 (t, *J* = 7.7 Hz, 2 H), 4.98 (dd, *J* = 1.1, 10.3 Hz, 1 H), 5.09 (dd, *J* = 1.1, 16.9 Hz, 1 H), 5.75 (dt, *J* = 15.0, 7.7 Hz, 1 H), 6.08 (dd, *J* = 10.3, 15.0 Hz, 1 H), 6.30 (dt, J = 16.9, 10.3 Hz, 1 H), 7.26 (d, *J* = 7.7 Hz, 1 H), 7.39 (dt, *J* = 1.1, 7.7 Hz, 1 H), 7.50 (dt, *J* = 1.1, 7.7 Hz, 1 H), 7.82 (dd, *J* = 1.1, 7.7 Hz, 1 H), 10.25 (s, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$, *E*-**2h**) δ 32.3, 34.7, 115.4, 126.5, 130.9, 131.8, 132.2, 133.3, 133.6, 136.8, 144.2, 192.1; ^{1}H NMR (400 MHz, $CDCl_3$, *Z*-**2h**) δ 2.52 (q, *J* = 8.0 Hz, 2 H), 3.30 (q, *J* = 8.0 Hz, 2 H), 5.07 (dd, *J* = 1.2, 8.5 Hz, 1 H), 5.17 (dd, *J* = 1.2, 16.8 Hz, 1 H), 5.50 (t, *J* = 8.5 Hz, 1 H), 6.02 (t, *J* = 8.5 Hz, 1 H), 6.54 (ddd, *J* = 1.2, 10.2, 16.8 Hz, 1 H), 7.29 (d, *J* = 6.8 Hz, 1 H), 7.43 (dt, *J* = 2.9, 6.8 Hz, 1 H), 7.45 (dt, *J* = 2.9, 6.8 Hz, 1 H), 7.67 (dd, *J* = 2.9, 6.8 Hz, 1 H),

10.25 (s, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$, *Z*-**2h**) δ 29.6, 32.4, 117.4, 128.5, 128.6, 130.2, 130.5, 130.6, 131.0, 132.2, 144.2, 192.1; HRMS calcd for $C_{13}H_{14}O$: 186.1045. Found *m/z* (relative intensity) 186.1048 (M^+, 49), 168 (12), 132 (31), 116 (100).

***cis*-1,2,2-Trimethyl-3-[(*1E*)-3-methyl-1,3-butadieny]cyclopentanecarbaldehyde** (**2i**): IR (neat) 3300 (w), 2900 (s), 2830 (m), 1700 (s), 1640 (w), 1600 (w), 1130 (w), 940 (m), 890 (w), 860 (m) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.80 (s, 3 H), 0.97 (s, 3 H), 1.09 (s, 3 H), 1.38 (ddd, *J* = 5.5, 9.2, 13.9 Hz, 1 H), 1.65 (dddd, *J* = 5.5, 9.2, 11.7, 13.9 Hz, 1 H), 1.93 (ddt, *J* = 4.7, 13.9, 9.2 Hz, 1 H), 2.43 (ddd, *J* = 4.7, 11.7, 13.9 Hz, 1 H), 2.52 (q, *J* = 9.2 Hz, 1 H), 4.91 (s, 2 H), 5.50 (dd, *J* = 9.2, 15.4 Hz, 1 H), 6.13 (d, *J* = 15.4 Hz, 1 H), 9.65 (s, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 18.7, 18.8, 19.4, 22.5, 27.6, 30.5, 47.6, 51.8, 58.3, 114.9, 129.5, 134.4, 141.8, 206.0; HRMS calcd for $C_{14}H_{22}O$: 206.1680. Found *m/z* (relative intensity): 206.1680 (M^+, 84), 191 (11), 135 (7), 121 (15), 110 (33), 109 (84), 95 (100), 79 (56).

***cis*-1,2,2-Trimethyl-3-[(1*E*,3*Z*)-1,3-pentadienyl]cyclopentanecarbaldehyde (2j):** IR (neat) 2980 (w), 2920 (m), 2840 (m), 2670 (w), 1720 (s), 1640 (w), 1470 (m), 1450 (m), 1410 (w), 1390 (m), 1370 (m), 980 (m) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.79 (s, 3 H), 0.97 (s, 3 H), 1.08 (s, 3 H), 1.38 (ddd, *J* = 5.5, 9.9, 13.9 Hz, 1 H), 1.68 (dddd, *J* = 5.5, 9.9, 11.7, 13.9 Hz, 1 H), 1.75 (dd, *J* = 1.8, 7.0 Hz, 3 H), 1.92 (ddt, *J* = 4.7, 13.9, 9.9 Hz, 1 H), 2.42 (ddd, *J* = 4.7, 11.7, 13.9 Hz, 1 H), 2.52 (dd, *J* = 8.4, 9.9 Hz, 1 H), 5.42 (dq, *J* = 11.0, 7.0 Hz, 1 H), 5.52 (dd, *J* = 8.4, 15.0 Hz, 1 H), 6.00 (ddd, *J* = 1.8, 11.0, 15.0 Hz, 1 H), 6.32 (dd, *J* = 11.0, 15.0 Hz, 1 H), 9.65 (s, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 18.7, 18.8, 19.4, 22.5, 27.6, 30.5, 47.6, 51.8, 58.3, 114.9, 129.5, 134.4, 141.8, 206.0; HRMS calcd for $C_{14}H_{22}O$: 206.1671. Found *m/z* (relative intensity) 206.1678 (M^+, 75), 191 (9), 122 (15), 107 (13), 95 (100).

***o*-[(*2E*)-4-Methyl-2,4-pentadienyl]benzaldehyde** (**2k**): IR (neat) 3040 (m), 3000 (m), 2920

(m), 2900 (m), 1700 (s), 1600 (s), 1180 (m), 1160 (w), 980 (s), 870 (m), 820 (w), 740 (m) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.81 (s, 3 H), 3.87 (d, J = 6.6 Hz, 2 H), 4.87 (br s, 1 H), 4.91 (br s, 1 H), 5.83 (dt, J = 15.8, 6.6 Hz, 1 H), 6.14 (d, J = 15.8 Hz, 1 H), 7.31 (d, J = 7.7 Hz, 1 H), 7.41 (dt, J = 1.5, 7.7 Hz, 1 H), 7.53 (dt, J = 1.5, 7.7 Hz, 1 H), 7.86 (dd, J = 1.5, 7.7 Hz, 1 H), 10.29 (s, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 18.0, 35.3, 126.6, 126.7, 128.3, 129.2, 130.8, 131.0, 131.4, 131.9, 133.8, 142.7, 192.1; HRMS calcd for $C_{13}H_{14}O$: 186.1045. Found m/z (relative intensity) 186.1054 (M^+, 93), 172 (13), 171 (100).

o*-[(*2E,4E*)-2,4-Hexadienyl]benzaldehyde** (**2*l): IR (neat) 3050 (m), 3000 (m), 2900 (w), 2825 (w), 1700 (s), 1600 (m), 1200 (m), 980 (m), 920 (w), 860 (w), 740 (m) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.72 (d, J = 6.6 Hz, 3 H), 3.81 (d, J = 6.6 Hz, 2 H), 5.60 (dq, J = 14.3, 6.6 Hz, 1 H), 5.73 (dt, J = 14.3, 6.6 Hz, 1 H), 5.97 (ddm, J = 9.9, 14.3 Hz, 1 H), 6.04 (ddm, J = 9.9, 14.3 Hz, 1 H), 7.29 (d, J = 7.7 Hz, 1 H), 7.39 (dt, J = 1.5, 7.7 Hz, 1 H), 7.51 (dt, J = 1.5, 7.7 Hz, 1 H), 7.83 (d, J = 7.7 Hz, 1 H), 10.26 (s, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 17.9, 35.2, 124.2, 126.6, 128.5, 129.1, 130.8, 131.0, 131.4, 131.9, 133.6, 142.7, 192.0; Anal. calcd for $C_{13}H_{14}O$: C, 83.83; H, 7.58. Found: C, 83.55; H, 7.65.

***o*-[(3*E*,5*E*)-5-phenyl-3,5-hexadienyl]benzaldehyde (2m):** IR (neat) 3063 (w), 3024 (w), 2932 (w), 1697 (s), 1597 (m), 1489 (w), 1450 (w), 1196 (m), 988 (s), 756 (s), 694 (m) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 2.46 (br q, J = 7.3 Hz, 2 H), 3.17 (t, J = 7.3 Hz, 2 H), 5.85 (dt, J = 15.1, 7.3 Hz, 1 H), 6.21 (ddd, J = 0.7, 10,5, 15.1 Hz, 1 H), 6.43 (d, J = 15.6 Hz, 1 H), 6.72 (dd, J = 10.5, 15.6 Hz, 1 H), 7.19 (t, J = 7.3 Hz, 1H), 7.27 (d, J = 7.6 Hz, 1 H), 7.28 (t, J = 7.3 Hz, 2 H), 7.36 (d, J = 7.3 Hz, 2 H), 7.38 (dt, J = 1.1, 7.6 Hz, 1 H), 7.50 (dt, J = 1.5, 7.6 Hz, 1 H), 7.82 (dd, J = 1.3, 7.6 Hz, 1 H), 10.25 (s, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 32.5, 35.0, 126.1, 126.5, 127.1, 128.4, 128.9, 130.6, 130.9, 131.4, 132.2, 133.6, 133.7, 137.4, 144.2, 192.1.

Methyl *o*-(3,5-Hexadienyl)phenyl ketone (2n): IR (neat) 3010 (w), 2930 (w), 2850 (w), 1690 (s), 1650 (w), 1600 (m), 1570 (m), 1490 (m), 1350 (s), 1250 (s), 1005 (s), 950 (m), 900 (m), 750 (s) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, *E*-**2n**) δ 2.36 (q, *J* = 7.7 Hz, 2 H), 2.58 (s, 3 H), 2.95 (t, *J* = 7.7 Hz, 2 H), 4.96 (dd, *J* = 1.1, 10.3 Hz, 1 H), 5.08 (dd, *J* = 1.1, 17.2 Hz, 1 H), 5.75 (dt, *J* = 15.0, 7.7 Hz, 1 H), 6.05 (dd, *J* = 10.3, 15.0 Hz, 1 H), 6.29 (dt, *J* = 17.2, 10.3 Hz, 1 H), 7.25 (dt, *J* = 1.1, 7.7 Hz, 1 H), 7.28 (dd, *J* = 1.1, 7.7 Hz, 1 H), 7.40 (dt, *J* = 1.1, 7.7 Hz, 1 H), 7.66 (dd, *J* = 1.1, 7.7 Hz, 1 H); ^1H NMR (400 MHz, $CDCl_3$, *Z*-**2n**) δ 2.48 (dq, *J* = 1.1, 7.7 Hz, 2 H), 2.59 (s, 3 H), 2.93 (t, *J* = 7.7 Hz, 2 H), 5.06 (d, *J* = 9.9 Hz, 1 H), 5.16 (dd, *J* = 1.1, 17.0 Hz, 1 H), 5.51 (dt, *J* = 9.9, 7.7 Hz, 1 H), 6.00 (t, *J* = 9.9 Hz, 1 H), 6.60 (ddt, *J* = 1.1, 9.9, 17.0 Hz, 1 H), 7.25 (dt, *J* = 1.1, 7.7 Hz, 1 H), 7.28 (dd, *J* = 1.1, 7.7 Hz, 1 H), 7.40 (dt, *J* = 1.1, 7.7 Hz, 1 H), 7.66 (dd, *J* = 1.1, 7.7 Hz, 1 H); HRMS calcd for $C_{14}H_{16}O$: 200.1201. Found *m/z* (relative intensity) 200.1201 (M^+, 2), 145 (29), 133 (55), 130 (100), 77 (15).

4-Phenyl-6,8-nonadienal (**2o**): IR (neat) 3025 (m), 2925 (m), 2825 (m), 2715 (w), 2360 (w), 1720 (s), 1650 (w), 1610 (w), 1005 (m), 905 (m), 765 (m), 700 (m) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, *E*-**2o**) *δ* 1.83 (m, 1 H), 2.07 (m, 1 H), 2.20 - 2.34 (dm, *J* = 1.5 Hz, 2 H), 2.35 - 2.47 (m, 2 H), 2.62 (ddt, *J* = 4.6, 11.7, 7.1 Hz, 1 H), 4.94 (d, *J* = 10.4 Hz, 1 H), 5.06 (d, *J* = 16.6 Hz, 1 H), 5.55 (dt, *J* = 14.9, 7.1 Hz, 1 H), 6.02 (dd, *J* = 10.4, 14.9 Hz, 1 H), 6.23 (dt, *J* = 16.8, 10.4 Hz, 1 H), 7.06 – 7.39 (m, 5 H), 9.64 (t, *J* = 1.5 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$, *E*-**2o**) *δ* 28.0, 40.0, 42.0, 45.4, 115.2, 126.4, 127.5, 128.4, 132.3, 132.6, 136.8, 143.6, 201.8; ^1H NMR (400 MHz, $CDCl_3$, *Z*-**2o**) *δ* 1.83 (m, 1 H), 2.07 (m, 1 H), 2.20 - 2.34 (dm, *J* = 1.5 Hz, 2 H), 2.35 - 2.47 (m, 2 H), 2.62 (m, 1 H), 5.05 (d, *J* = 10.0 Hz, 1 H), 5.16 (d, *J* = 16.6 Hz, 1 H), 5.34 (q, *J* = 7.9 Hz, 1 H), 5.98 (dd, *J* = 7.9, 10.0 Hz, 1 H), 6.57 (dt, *J* = 16.6, 10.0 Hz, 1 H), 7.06 – 7.39 (m, 5 H), 9.64 (t, *J* = 1.5 Hz, 1 H); HRMS calcd for $C_{15}H_{18}O$: 214.1358. Found *m/z* (relative intensity): 214.1323 (M^+, 100), 215 (19), 197 (3), 196 (75), 170 (13).

4-*tert*-Butyl-6,8-nonadienal (2p): IR (neat) 3420 (br m), 2960 (s), 2870 (m), 2720 (w), 1720 (s), 1650 (w), 1600 (w), 1470 (m), 1390 (m), 1360 (s), 1010 (s), 950 (m) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, *E*-**2p**) δ 0.90 (s, 3 H), 1.12 (tt, *J* = 4.0, 8.1 Hz, 1 H), 1.41 (m, 1 H), 1.81-1.95 (m, 2 H), 2.31-.2.44 (m, 2 H), 2.53 (dddd, *J*= 1.5, 5.9, 9.5, 17.2 Hz, 1 H), 4.96 (d, *J* = 10.2 Hz, 1 H), 5.08 (d, *J* = 16.9 Hz, 1 H), 5.67 (ddd, *J* = 5.9, 9.5, 15.0 Hz, 1 H), 6.03 (dd, *J* = 10.3, 15.0 Hz, 1 H), 6.29 (dt, *J* = 16.9, 10.3 Hz, 1 H), 9.72 (t, *J* = 1.6 Hz, 1 H); HRMS calcd for $C_{13}H_{22}O$: 194.1671. Found *m/z* (relative intensity) 194.1684 (M^+, 68), 140 (15), 137 (20), 109 (100), 106 (50), 95 (25).

1-(Formylmethyl)-2-(4'-methyl-2',4'-pentadienyl)cyclohexane (**2q**): IR (neat) 2910 (s), 2840 (s), 2690 (m), 1725 (s), 1650 (w), 1000 (s), 950 (w), 900 (m), 860 (m) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, *E*-**2q**) *δ* 1.24 - 1.72 (m, 10 H), 2.00 (t, *J* = 7.7 Hz, 2 H), 2.35 (dm, *J* = 2.2 Hz, 2 H), 4.97 (d, *J* = 10.3 Hz, 1 H), 5.08 (d, *J* = 16.9 Hz, 1 H), 5.63 (dt, *J* = 15.0, 7.7 Hz, 1 H), 6.03 (dd, *J* = 10.3, 15.0 Hz, 1 H), 6.29 (dt, *J* = 16.9, 10.3 Hz, 1 H), 9.70 (t, *J* = 2.2 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$, *E*-**2q**) *δ* 22.7, 23.7, 28.1, 29.4, 33.1, 39.3, 39.6, 43.9, 114.9, 130.2, 132.2, 136.9, 202.7; ^1H NMR (400 MHz, $CDCl_3$, *Z*-**2q**) *δ* 1.24 - 1.72 (m, 10 H), 2.00 (t, *J* = 7.7 Hz, 2 H), 2.35 (dm, *J* = 2.2 Hz, 2 H), 5.08 (d, *J* = 16.9 Hz, 1 H), 5.19 (d, *J* = 16.9 Hz, 1 H), 5.40 (dt, *J* = 10.3, 7.7 Hz, 1 H), 6.05 (t, *J* = 10.3Hz, 1 H), 6.60 (dt, *J* = 16.9, 10.3 Hz, 1 H), 9.70 (t, *J* = 2.2 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$, *Z*-**2q**) *δ* 25.9, 28.2, 29.0, 31.8, 34.1, 36.7, 41.7, 48.5, 117.2, 130.9, 131.9, 133.3, 202.6; HRMS calcd for $C_{13}H_{20}O$: 192.1514. Found *m/z* (relative intensity): 192.1519 (M^+, 48), 174 (9), 138 (99), 81 (100).

8,10-Undecadienal (**2r**): IR (neat) 3400 (m), 2920 (s), 2850 (s), 2720 (m), 1730 (s), 1650 (w), 1000 (m), 900 (s), 780 (m) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, *Z*-**2r**) *δ* 1.31 - 1.45 (m, 5 H), 1.60 - 1.68 (m, 3 H), 2.18 (qm, *J* = 7.3 Hz, 2 H), 2.41 (dt, *J* = 1.8, 7.3 Hz, 2 H), 5.08 (d, *J* = 10.6 Hz, 1 H), 5.18 (br d, *J* = 16.9 Hz, 1 H), 5.43 (dd, *J* = 7.3, 10.6 Hz, 1 H), 5.99 (t, *J* = 10.6

Hz, 1 H), 6.62 (dt, *J* = 16.9, 10.6 Hz, 1 H), 9.76 (t, *J* = 1.8 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$, *Z*-**2r**) δ 22.0, 27.6, 28.8, 28.9, 29.0, 43.8, 116.6, 129.1, 132.2, 132.5, 202.4; ^{1}H NMR (400 MHz, $CDCl_3$, *E*-**2r**) δ 1.31 - 1.45 (m, 5 H), 1.60 - 1.68 (m, 3 H), 2.08 (qm, *J* = 7.3 Hz, 2 H), 2.26 (t, *J* = 7.7 Hz, 2 H), 4.95 (d, *J* = 10.3 Hz, 1 H), 5.09 (d, *J* = 16.8 Hz, 1 H), 5.69 (dt, *J* = 7.0, 14.7 Hz, 1 H), 6.08 (dd, *J* = 10.3, 14.7 Hz, 1 H), 6.30 (dt, *J* = 16.8, 10.3 Hz, 1 H), 9.76 (t, *J* = 1.8 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$, *E*-**2r**) δ 27.7, 28.8, 28.9, 28.9, 29.0, 32.4, 116.6, 129.1, 132.2, 132.5, 195.0; HRMS calcd for $C_{11}H_{18}O$: 166.1358. Found *m/z* (relative intensity): 166.1356 (M^+, 55), 137 (13), 123 (12), 111 (10), 98 (100), 93 (20), 83 (14), 67 (70).

(*12E*)-14-Methyl-12,14-pentadecadienal (**2t**): IR (neat) 2920 (s), 2840 (s), 1730 (s), 1610 (m), 960 (s), 870 (m) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.25 - 1.43 (m, 14 H), 1.58 - 1.71 (m, 2 H), 1.83 (t, *J* = 1.1 Hz, 3 H), 2.09 (q, *J* = 7.0 Hz, 2 H), 4.86 (s, 2 H), 5.66 (dt, *J* = 3.3, 7.0 Hz, 1 H), 6.13 (d, *J* = 15.4 Hz, 1 H), 9.76 (t, *J* = 1.8 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 18.7, 22.1, 29.1, 29.2, 29.3, 29.4, 29.5, 29.6, 29.7, 32.7, 43.9, 113.9, 130.9, 132.6, 142.1, 202.6; Anal. calcd for $C_{16}H_{28}O_3$: C, 81.29; H, 11.94. Found: C, 81.29; H, 11.95.

***cis*-1,2,2-Tirmethyl-3-[(1*E*,3*Z*)-3-methylpenta-1,3-dienyl]cyclopentanecarbaldehyde (2u):** IR (neat) 2950 (s), 2880 (m), 2700 (w), 1760 (m), 1720 (s), 1450 (m), 1370 (m), 960 (w), 900 (w), 840 (w), 780 (w) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.80 (s, 3 H), 0.96 (s, 3 H), 1.08 (s, 3 H), 1.37 (ddd, *J* = 5.5, 9.2, 13.9 Hz, 1 H), 1.65 (dddd, *J* = 5.5, 9.2, 11.7, 13.9 Hz, 1 H), 1.71 (dd, *J* = 1.5, 7.0 Hz, 1 H), 1.80 (t, *J* = 1.5 Hz, 3 H), 1.92 (ddt, *J* = 5.1, 13.9, 9.2 Hz, 1 H), 2.43 (ddd, *J* = 5.1, 11.7, 13.9 Hz, 1 H), 2.50 (q, *J* = 9.2 Hz, 1 H), 5.34 (q, *J* = 7.0 Hz, 1 H), 5.48 (dd, *J* = 9.2, 15.4 Hz, 1 H), 6.41 (d, *J* = 15.4 Hz, 1 H), 9.66 (s, 1 H). NOE: C3*'Me* (8.3%) by irradiation at C1'H; C4'*Me* (14.6%) and C4'H (0%) by irradiation at C2'H; HRMS calcd for $C_{15}H_{24}O$: 220.1827. Found *m/z* (relative intensity) 220.1827 (M^+, 100), 205 (10), 192 (45), 177 (43), 152 (31), 109 (88), 108 (53).

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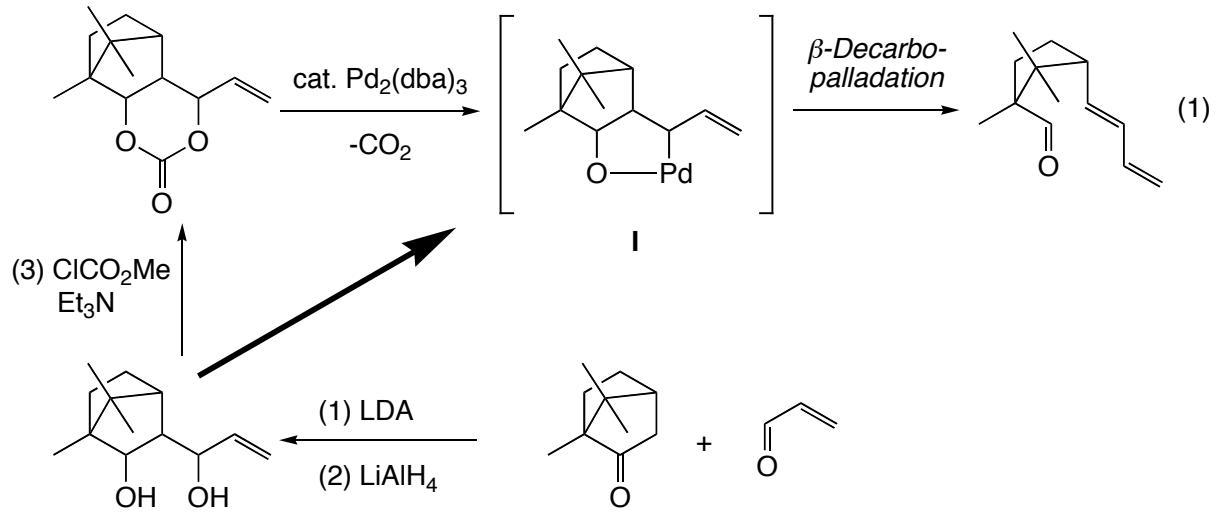
第２章

パラジウム触媒、有機ホウ素を用いる４－ペンテン－１，３－ジオール誘導体の炭素－炭素結合切断反応の開発

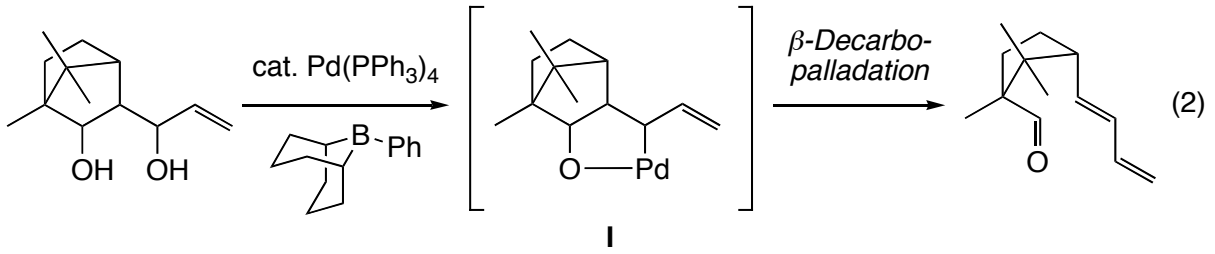
２－１　緒言

前章で述べたように、パラジウム触媒を用いて４－ビニル環状カーボネートを反応させると、Pd(0)のアリル C－O 結合への酸化的付加及び脱炭酸が起こり、π－アリルパラジウム中間体 **I** を形成し、β-decarbopalladation による炭素－炭素結合切断反応を受けてω－ジエニルアルデヒドを与える（式１）。[1]



この反応は、４－ペンテン－１，３－ジオールを環状カーボネートに活性化する必要がある。環状カーボネートは、シクロアルカノンとα，β－不飽和アルデヒドの交差アルドール反応、$LiAlH_4$ 還元によるジオールの生成、クロロ炭酸メチルによる環化で合成できる。ところが、ジオールから環状カーボネートへの変換反応は、大過剰

のクロロ炭酸メチル、トリエチルアミンを必要とし、さらに、基質の構造次第で極めて低収率の場合もあり大きな問題であった。[1],[2] ジオールから直接ω－ジエニルアルデヒドに誘導できれば、この変換反応の有用性は大幅に向上する。当研究室では、トリエチルホウ素がアリルアルコールから直接的にπ－アリルパラジウムを発生する促進剤として作用し、様々な炭素－炭素結合形成反応に適用できることを報告している。[3] この知見を基に検討を行った結果、パラジウム触媒、9-phenyl-9-borabicyclo[3.3.1]nonane（9-Ph-9-BBN）[4]を促進剤として用いると、環状カーボネートの前駆体である４－ペンテン－１，３－ジオールの炭素－炭素結合切断反応が進行し、ω－ジエニルアルデヒドを与えることを発見した（式２）。



I

本反応は、9-Ph-9-BBN が Lewis 酸として作用して、アリルアルコール部位を活性化する。そして、アリルアルコールから直接的にπ－アリルパラジウム中間体 **I** が発生し、β-decarbopalladation が起こると考えられる。本反応は、反応機構の観点から興味深いだけではなく、ジオールを環状カーボネートに誘導せず、直接用いることができる点で合成的メリットが大きい。また、生成物のω－ジエニルアルデヒドは、変換しやすい官能基ジエン、アルデヒドを有する化合物であり天然物合成の戦略的合成中間体として有用である。[1b] さらに副生成物は水である。以上のことから、本反応は、高効率、低コストであり、また、環境の面からも注目に値する。

本章では、パラジウム触媒、有機ホウ素を用いる４－ペンテン－１，３－ジオール誘導体の炭素－炭素結合切断反応の反応性及び選択性について報告する。

２－２　結果及び考察

２－２－１　反応条件の検討

有機ホウ素の検討を行った。常圧窒素雰囲気下、テトラキス（トリフェニルホスフィン）パラジウム（０）、４－ペンテン－１，３－ジオール **1u**（0.5 mmol）、各種溶媒（2.5 ml）を用いて反応を行った。その結果を Table 1 に示す。

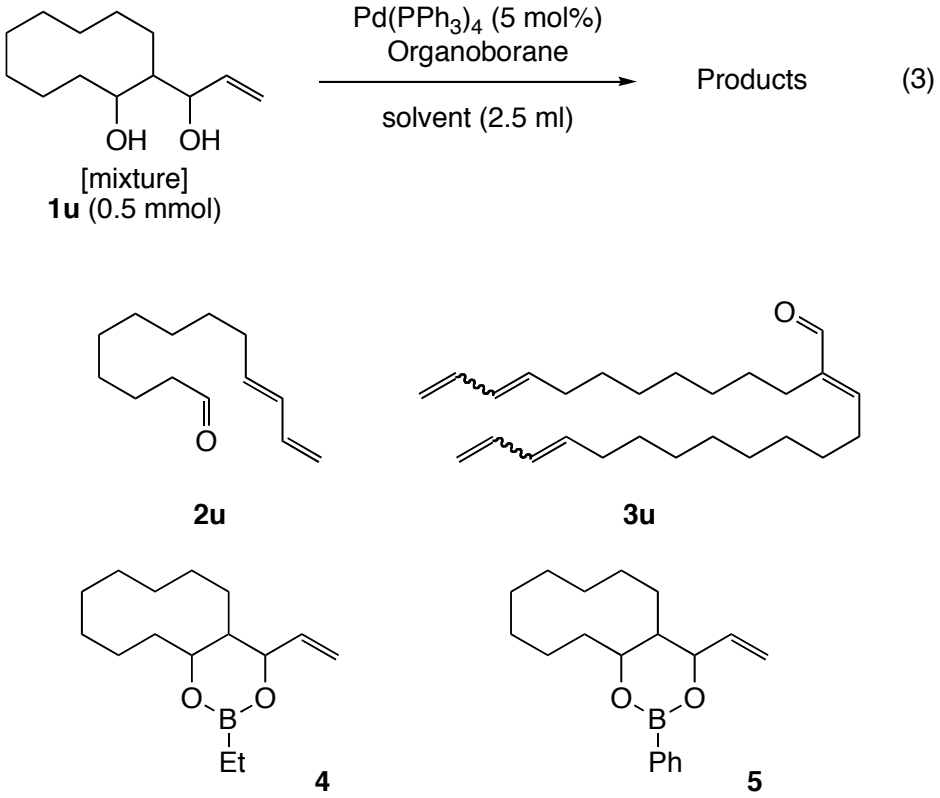


Table 1. Palladium-Catalyzed C-C Bond Cleavage Reaction of 4-Penten-1,3-diol **1u** Promoted by Organoborane

Run	Organoborane (equiv.) / Solvent	Condition	Products % Isolated yield
1[a]	Et_3B (3.6) / THF	r.t., 24 h	**4**: 43
2[a]	Et_3B (3.6) / toluene	110 ºC, 24 h	**4**: 64
3[b,c]	Et_3B (3.6) / MeCN	81 ºC, 24 h	**2u**: 15 [*E* : *Z* = 3 : 1] **4**: 48

(Table 1 continued.)

4[a]	Ph_3B [THF] (3.6) / THF	r.t., 24 h	**2u**: 5 [*E* : *Z* = 4 : 1] **5**: 12
5[a]	Ph_3B [THF] (3.6) / toluene	110 ºC, 24 h	**2u**: 12 [*E* : *Z* = 3 : 1] **5**: 64
6[b,c]	Ph_3B [THF] (3.0) / THF	55 ºC, 35 h	**2u**: 16 [*E* : *Z* = 5 : 1] **5**: 55
7[b,d]	Ph_3B [THF] (1.2) / THF	55 ºC, 24 h	**2u**: 16 [*E* : *Z* = 4 : 1] **5**: 71
8[b]	$(C_6F_5)_3B$ (1.2) / THF	55 ºC, 60 h	No Reaction
9[b]	$Ph_4B^-Na^+$ (3.0) / THF	50 ºC, 3 h	No Reaction
10[a]	*B*-Ph-9-BBN[e] (1.2) / toluene	50 ºC, 12 h	**2u**: 15 [*E* : *Z* = 4 : 1] **3u**: 54 [*E* : *Z* = 5 : 1]
11[a]	*B*-Ph-9-BBN (0.5) / toluene	50 ºC, 45 h	**2u**: 20 (23)[f] [*E* : *Z* = 3 : 1] **3u**: 55 (64)[f] [*E* : *Z* = 3 : 1]

[a] $Pd(PPh_3)_4$ (5 mol%) was used. [b] $Pd(PPh_3)_4$ (10 mol%) was used.
[c] Et_3N (3.6 equiv.) was added. [d] K_3PO_4 (1.2 equiv.) was added.
[e] *B*-Ph-9-BBN [prepared from *B*-MeO-9-BBN (0.25 mmol, in THF) and PhLi (0.25 mmol in ether)]
[f] Conversion yield.

トリエチルホウ素を用いた場合、室温で瞬時にホウ酸エステル **4** を形成し、炭素－炭素結合切断反応は進行しなかった（Run 1）。トルエン還流下で反応を行ったが同様の結果を与えた（Run 2）。トリエチルアミンを添加し、アセトニトリル還流下で反応を行うと、主に **4** を形成したが、低収率でω－ジエニルアルデヒド **2u** を与えた（Run 3）。トリフェニルホウ素の場合は、ホウ酸エステル **5** の形成が優先したが、炭素－炭素結合切断反応の進行が見られ、低収率ながら **2u** を与えた（Run 4）。高温、塩基存在下で反応を行ったが殆ど変化は見られなかった（Runs 5-7）。$(C_6F_5)_3B$ や $Ph_4B^-Na^+$では全く反応しなかった（Runs 8 and 9）。ホウ酸エステルの形成を妨げるために、ビシクロ系を持ち、加水分解されにくいと予想される 9-phenyl-9-borabicyclo[3.3.0]nonane（9-Ph-9-BBN）[4]を用いると、期待どおり炭素－炭素結合切断反応が優先的に進行したが、**2u** が更に自己アルドール縮合した **3u** を主生成物とし

て与えた（Run 10）。9-Ph-9-BBN を 50 mol%まで減らしても同様の結果を与えた（Runs 11）。

２－２－２　４－ペンテン－１，３－ジオール誘導体の検討

常圧窒素雰囲気下、$Pd(PPh_3)_4$（0.025 mmol）、9-Ph-9-BBN（0.5 mmol）、４－ペンテン－１，３－ジオール **1**（0.5 mmol）、トルエン（2.5 ml）を用いて反応を行った。その結果を Table 2 に示す。また、**1** の総収率（Aldol 反応、LAH 還元）並びに環化収率（$ClCO_2Me$ または Im_2CO による環化）を示す。

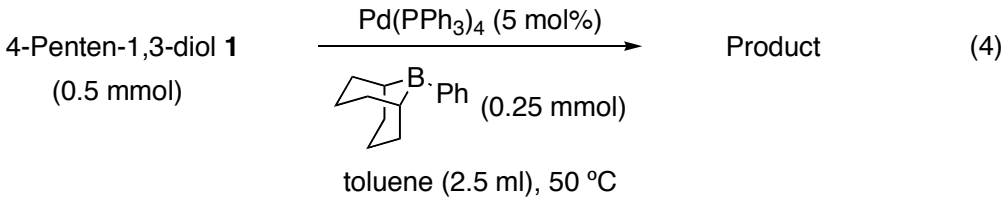
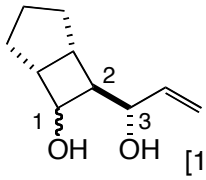
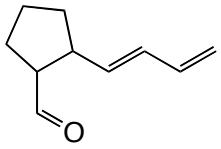
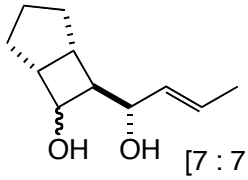
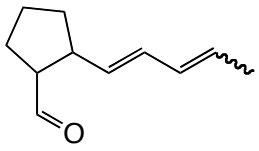
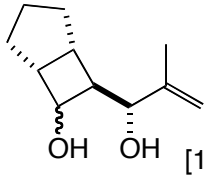
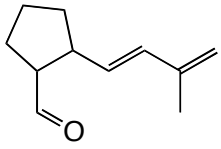
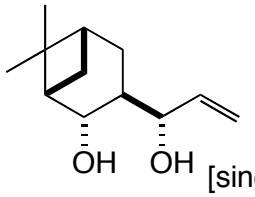
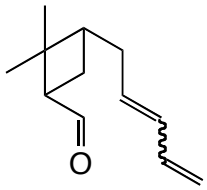
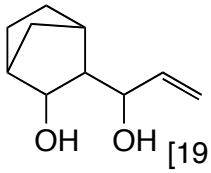
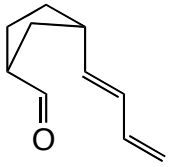
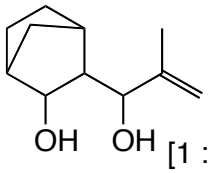
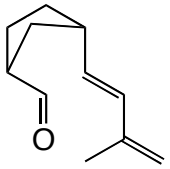
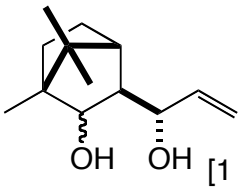
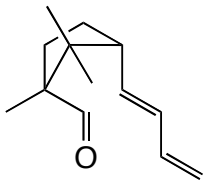
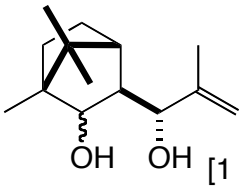
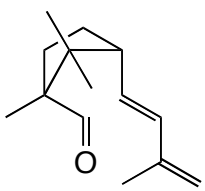


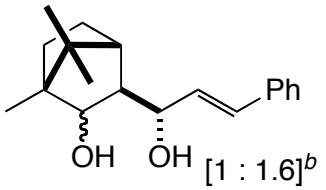
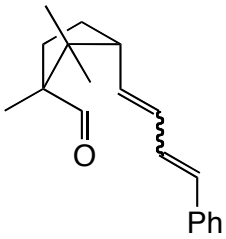
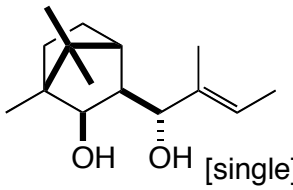
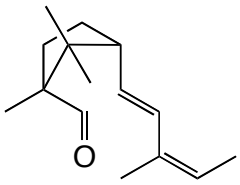
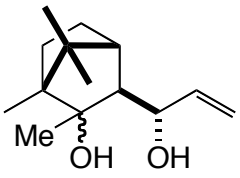
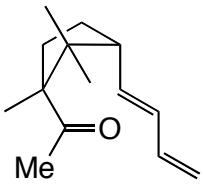
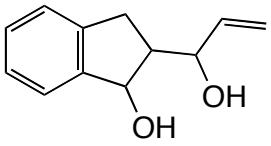
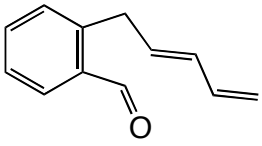
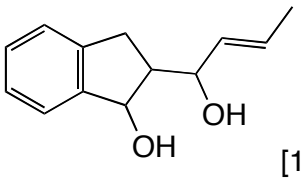
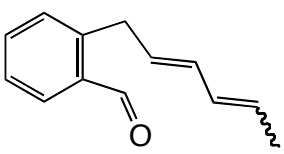
Table 2. Palladium-Catalyzed C-C Bond Cleavage Reaction of 4-Penten-1,3-diols **1** Promoted by *B*-Ph-9-BBN

Run	4-Penten-1,3-diol **1** [Stereoisomer ratio] (Aldol, LAH reduction, Carbonation[f,g])	Time (h)	Product	% yield [*E* : *Z*][a]
1	 **1a** [1 : 1][b] (100, 78, 54[f])	12		**2a**: 87 [11 : 1]
2	 **1b** [7 : 7 : 6 : 1] (63, 93, no data)	24		**2b**: 80 [2 : 1][c]
3	 **1c** [1 : 1][b] (30, 63, no data)	24		**2c**: 68 (78)[e] [only *E*]

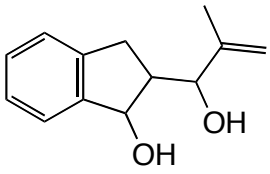
(Table 2, continued.)

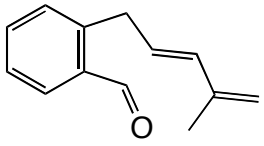
4	 **1d** (98, 85, 0[g])	[single]	24		**2d**: 92 [1 : 1]
5	 **1e** (86, 88, 17[g])	[19 : 6 : 1]	24		**2e**: 81 [4 : 1]
6	 **1f** (52, 57, no data)	[1 : 1]	50 ºC, 12 h 80 ºC, 1 h		**2f**: 58 (75)[e] [only *E*]
7	 **1g** (96, 83, 60[f]/73[g])	[1 : 3][b]	2		**2g**: 94 [only *E*]
8	 **1h** (100, 95, 62[f]/54[g])	[1 : 4][b]	48		**2h**: 78 [only *E*]

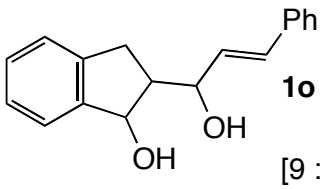
(Table 2, continued.)

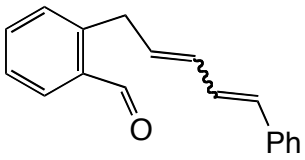
9	 [1 : 1.6][b] (100, 95, 32[f]/0[g])	**1i**	50 ºC, 27 h 80 ºC, 2 h		**2i**: 75 [7 : 1][d]
10	 [single] (100, 95, 32[f]/77[g])	**1j**	50 ºC, 36 h 110 C, 3 h		**2j**: 38 (54)[e] [only *E,Z*]
11	 [1 : 7][b] (100, 22[h], 100[f])	**1k**	24		**2k**: 70 [only *E*]
12	 [2 : 2 : 1] (85, 89, 84[f]/54[g])	**1*l***	24		**2*l***: 25 (39)[e] [8 : 1]
13	 [1 : 1 : 1] (96, 100, 87[f])	**1m**	30		**2m**: 56 [4 : 1][c]

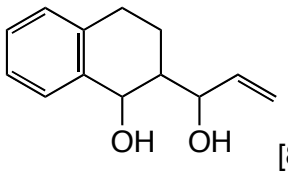
(Table 2, continued.)

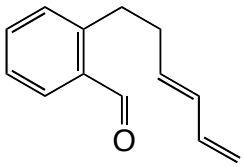
14  **1n** [2 : 2 : 1]
(100, 89, 57[f], 76[g])

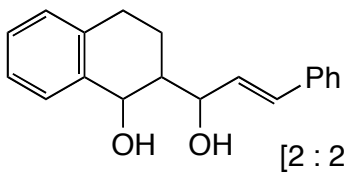
45  **2n**: 38 [only *E*]

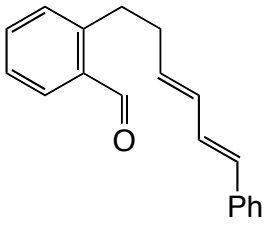
15  **1o** [9 : 5 : 2 : 1]
(97, 67, no data)

48  **2o**: 20 (32)[e] [3 : 1][d]

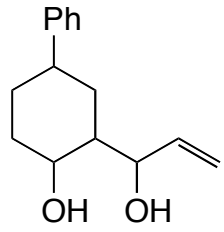
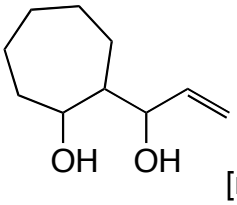
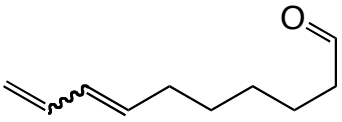
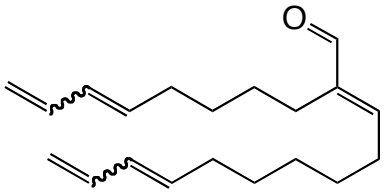
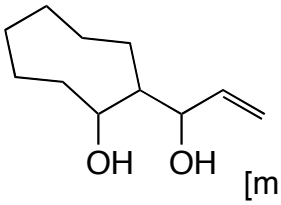
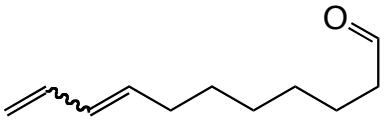
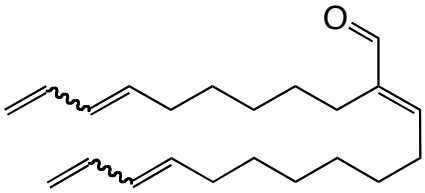
16  **1p** [8 : 4 : 2 : 1]
(96, 100, 92[f]/68[g])

6  **2p**: 28 [only *E*]

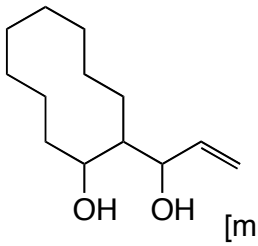
17  **1q** [2 : 2 : 1]
(98, 84, 22[g])

48  **2q**: trace

(Table 2, continued.)

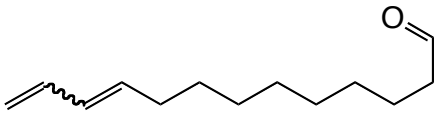
18	 [mixture] (70, 100, 19[f])	**1r**	36	No Reaction
19	 [mixture] (80, 92, no data)	**1s**	48	 **2s**: 1  **3s**: 59 [7 : 1]
20	 [mixture] (100, 91, 93[f])	**1t**	24	 **2t**: 15 [5 : 1]  **3t**: 54 [3 : 1]

(Table 2, continued.)

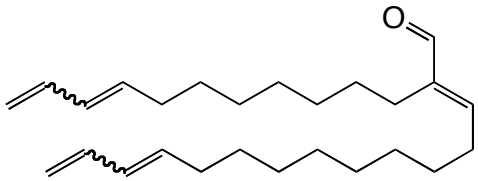
21  **1u**

[mixture]

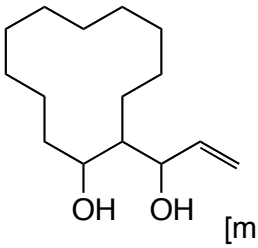
(94, 96, 54[f])

45 

2u: 20 (23)[e] [3 : 1]

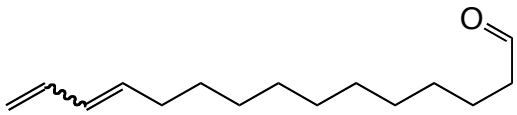


3u: 55 (64)[e] [3 : 1]

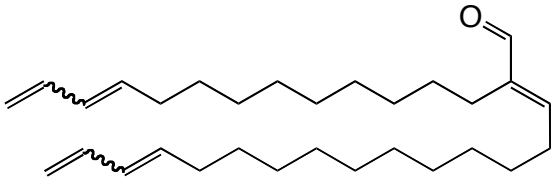
22  **1v**

[mixture]

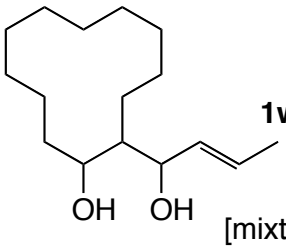
(100, 97, 78[f])

24 

2v: 27 [3 : 1]



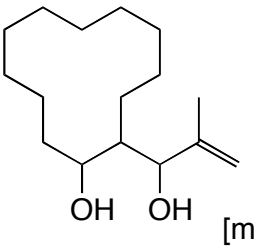
3v: 33 [2 : 1]

23  **1w**

[mixture]

(100, 100, 50[f])

36 No Reaction

24  **1x**

[mixture]

(100, 81, 98[f])

50 ºC, 18 h
110 ºC, 18 h

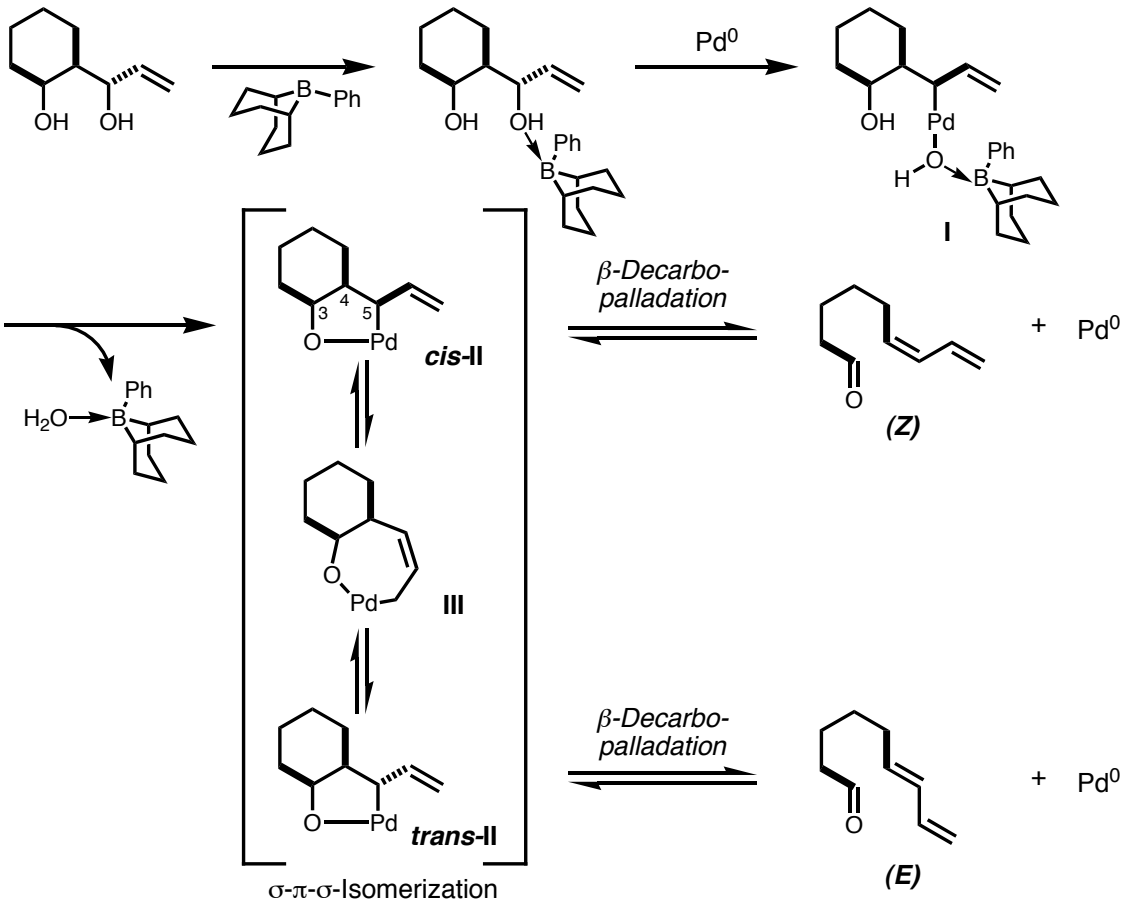
No Reaction

[a] Geometrical isomers were not separable by means of conventional column chromatography, and the isomers ratio were determined on the basis of ^{1}H NMR (400 MHz). [b] syn/anti ratio regarding C1 and C3 hydroxyl groups. [c] *EE*/*EZ* ratio. [d] *EE*/*ZE* ratio. [e] Conversion yield.
[f] $ClCO_2Me$ (7.0 equiv.), Et_3N (8.5 equiv.) was used in CH_2Cl_2 at r.t..
[g] 1,1'-Carbonyldiimidazole (2.0 equiv.) was used in THF at r.t..
[h] MeLi (2.5 equiv.) was used in ether at r.t..

本反応は、環のひずみが大きい基質に関して良好な結果を与えた。シクロブタノール骨格を有する **1a**-**1c** を用いた反応は、高い *E* 選択性を示し、高収率で **2a**-**2c** を与えた（Runs 1-3）。**1a**-**1c** はいずれも C1 炭素の水酸基と、C2 炭素のアリルアルコール部位が *cis* 及び *trans* の立体異性体の混合物である。*trans* 体のジオール **1a**-**1c** の環状カーボネートへの誘導は立体的に困難であり、従来法では *trans* 体のジオール **1a**-**1c** を反応に用いることはできなかった。本反応は、反応基質の立体化学の如何を問わず、立体選択的に炭素－炭素結合切断反応が進行することから非常に有用性が高い。C2 炭素のメチレン基と C3 炭素のビニル基が *trans* である **1d** の場合には、高収率で **2d** を与えた。この際、ジエン部位の *E*、*Z* 比は１：１であった（Run 4）。**1e** を用いた反応では、**2e** を *E* 選択的に、かつ高収率で与えた（Run 5）。オレフィン部位の内部炭素にメチル基が置換した **1f** は、中程度の収率で *E* 体の **2f** を与えた（Run 6）。**1g** を用いた場合には、速やかに反応が進行し、高収率で *E* 体の **2g** を与えた（Run 7）。**1g** のオレフィン部位が置換した **1h**、**1i** を用いた場合では、反応時間は長くなるが、良好な収率で、かつ立体選択的に **2h**、**2i** を与えた（Runs 8 and 9）。ところが、**1j** は殆ど反応せず、低収率で **2j** を与えた（Run 10）。反応時間、収率から判断して、オレフィン部位の置換基は反応を阻害する傾向があると考えられる。また、本反応は、ω－ジエニルケトンの合成にも適用でき、**1k** を反応させると *E* 体の **2k** を良好な収率で与えた（Run 11）。シクロペンタン誘導体 **1*l*** を用いた場合には、反応は複雑になり、低収率で **2*l*** を与えた（Run 12）。**1m** の場合には、良好な収率で **2m** を与えたが（Run 13）、**1n**、**1o** は低収率で **2n**、**2o** を与えた（Runs 14 and 15）。環のひずみが

ないシクロヘキサン誘導体 **1p**、**1q** を用いた場合には、反応は完結せず複雑になり、低収率で **2p**、**2q** が得られた（Runs 16 and 17）。**1r** を用いた場合には、反応は進行しなかった（Run 18）。本反応は、4 員環、5 員環のみならず、tosional strain が大きい、7 員環 **1s** 、8 員環 **1t**、10 員環 **1u**、そして 12 員環 **1v** の環の切断反応にも適用できたが、生成したωージエニルアルデヒド **2s**-**2v** が更に自己アルドール縮合した **3s**-**3v** を与えた（Runs 19-22）。**1w**、**1x** に至っては、炭素－炭素結合切断反応が進行しなかった（Runs 23 and 24）。

炭素－炭素結合切断反応における立体選択性から判断して、次の反応機構を推定した（Scheme 1）。

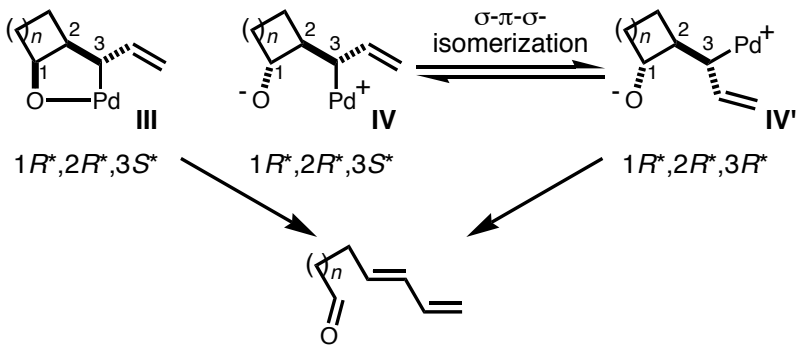


Scmeme 1. Plausible Reaction Mechanism for the Palladium-Catalyzed C-C Bond Cleavage Reaction.

C2 炭素の置換基と C3 炭素のビニル基がトランスの関係にある４－ペンテン－１，３－ジオール誘導体を例に説明する。9-Ph-9-BBN はルイス酸として作用し、アリルアルコールの酸素原子に配位して、アリルアルコール部位を活性化すると思われる。アリル C－O 結合への Pd(0)の酸化的付加が立体反転で進行し、π-アリルパラジウム中間体 **I** を形成する。水，9-Ph-9-BBN が脱離し、オキサパラダサイクル *cis*-**II** を形成する。*cis*-**II** から直接β-decarbopalladation による C3－C4 結合の切断と同時に Pd(0)が再生すると、Z 体のω－ジエニルアルデヒドを与える。もう一つのルートとして、*cis*-**II** の C5 位のビニル基と環の立体反発を避けるようにσ－π－σ異性化が起こり、熱力

学的により安定な *trans*-**II** に変換し、β-decarbopalladation が進行すると *E* 体のω－ジエニルアルデヒドを与える。

４－ペンテン－１，３－ジオール **1a** の C1 炭素の水酸基と C2 炭素のアリルアルコール部位が *trans* の立体異性体（***trans*-1a**）は、炭素－炭素結合切断反応を受け、*E* 体のω―ジエニルアルデヒド**(*E*)-2a** を選択的に与える（Table 2, Run 1）。***trans*-1a** からオキサパラダサイクルを形成すると *trans* ビシクロ[3.2.0]系となり、その形成はひずみの為に極めて困難であると考えられる。従って Scheme 2 に示すような非環状のπ－アリルパラジウム中間体 **IV** (*n* = 1)を介して炭素－炭素結合切断反応が進行することも考えられる。



Scmeme 2. Plausible Reaction Mechanism for the Palladium-Catalyzed C-C Bond Cleavage Reaction.

このように本研究では、４－ペンテン－１，３－ジオールの炭素－炭素結合切断反応がパラジウム触媒、9-Ph-9-BBN を促進剤として用いると容易に進行することを見出した。最も重要なことは、ジオールを環状カーボネートに誘導する必要がなく、直接反応に用いることができ、合成的メリットが高いことである。反応条件の温和さ、４員環、５員環のみならず、１２員環の環切断反応に適用できること、反応基質の立体化学によらず反応が進行すること、生成物のω－ジエニルアルデヒドの合成反応中間体としての有用性、そして、副生成物が水であることから、本反応は、高効率有機合成や環境調和型有機合成の観点から注目に値し、精密有機合成並びに天然物合成の分野で強力な合成手法に成り得ることが期待される。

Experimental Section

Reactions employed oven-dried glassware unless otherwise noted. Thin layer chromatography (TLC) employed glass 0.25 mm silica gel plates with UV indicator (Merck, Silica gel $60F_{254}$). Flash chromatography columns were packed with silica gel (Wakogel-C300) as a slurry in hexane. Gradient flash chromatography was conducted eluting with a continuous gradient from hexane to the indicated solvent. Proton and carbon NMR data were obtained with a JEOL-GX400 with tetramethylsilane as an internal standard. Chemical shift values were given in ppm downfield from the internal standard. Infrared spectra were recorded with a JASCO A-100 FT-IR spectrophotometer. High resolution mass spectra (HRMS) were measured with a JEOL JMS-DX303. Combustion analyses were performed by the Instrumental Analysis Center of Nagasaki University. Analysis agreed with the calculated values within $\pm$ 0.4%.

Solvents and Reagents. Tetrahydrofuran and ether were distilled from a blue solution of sodium benzophenone ketyl under N_2 immediately prior to use. Toluene was distilled under nitrogen from calcium hydride. $Pd(PPh_3)_4$ (Nakalai tesque, Inc.), *B*-methoxy-9-BBN (1.0 M solution in hexanes, Aldrich), PhLi (1.0 M solution in cyclohexane-diethyl ether solution, Kanto Chemical, Co., Inc.) were purchased and used without further purification. 4-Penten-1,3-diols **1a** – **1x** were prepared according to the method reported previously from our laboratories. [1],[2],[5],[6] One typical example is shown below.

Preparation of 4-Penten-1,3-diol (**1d**): A solution of β-pinene (2.4 mL, 15 mmol) in a mixture of methanol (8 mL) and dichloromethane (8 mL) was cooled to –78 ºC in a nitrogen purged Schlenk flask. While the mixture was stirred at the same temperature, ozone was bubbled through the solution by means of a sinter-glass-ended tube for 3 h, until the blue color

persisted. The reaction progress was monitored by TLC (hexane/AcOEt = 95:5, v/v). Nitrogen was then bubbled through the reaction mixture for 1 h, which was then allowed to warm to room temperature. Zinc powder (2.9 g, 45 mmol, 3 equiv.) and acetic acid (4.2 mL, 75 mmol, 5 equiv.) were then added carefully, portionwise, over 1 h period. The resulting suspension was filtered and the solid was washed with dichloromethane repeatedly. The organic layer was carefully washed with saturated aqueous $NaHCO_3$ solution. The aqueous layer was extracted with dichloromethane. The combined organic layer was washed with water, dried over $MgSO_4$ and the solvent was evaporated *in vacuo*. The residue was purified by distillation (100 ºC/20 mmHg) to give nopinone in 91% yield. [7]

A 200 mL of three-necked round-bottomed flask, equipped with a dropping funnel, a rubber septum, and an air condenser at the top of which is attached a three-way stopcock fitted a nitrogen balloon, is charged with freshly distilled THF (10 mL) and diisopropylamine (0.8 mL, 5.5 mmol) via syringe under nitrogen. Into the flask was added *n*-butyllithium (3.4 mL, 5.5 mmol; 1.6 M hexane solution) at -78 ˚C, and the mixture was stirred for 1 hour. To the reaction mixture was added nopinone (0.69 g, 5 mmol) dissolved in THF (10 mL) via dropping funnel at -78 ˚C, and the mixture was stirred at 0 ˚C for 1 h. A solution of acrolein (0.4 mL, 6 mmol) in dry THF (10 mL) was quickly added at -78 ˚C and stirred for 1 minute. The reaction mixture was quenched by 2M HCl at -78 ˚C and extracted with ethyl acetate (2 x 30 mL). The organic extracts were washed with sat. $NaHCO_3$ and sat. NaCl, and the combined extracts were dried ($MgSO_4$). The solvent was removed *in vacuo*, and the residue was subjected to column chromatography on silica gel (hexane/ethyl acetate = 8:1, v/v) to give the aldol product in 98% yield.

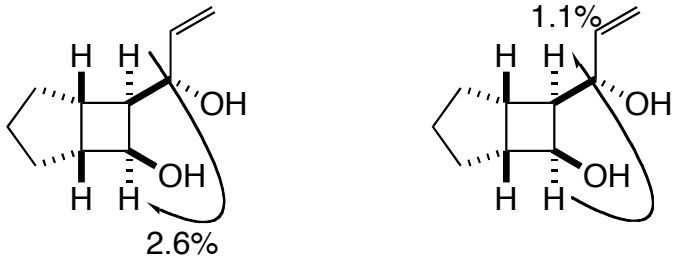
Into a suspension of lithium aluminum hydride (0.28 g, 7.4 mmol) in ether (20 mL) was added the aldol product (0.95 g, 4.9 mmol) dissolved in dry ether (10 mL) at 0 ˚C. After stirring for 30 min at the same temperature, the excess lithium aluminum hydride was decomposed by adding aqueous THF (THF/water = 1:1, v/v) dropwise until gray slurry turned

into white granules. After filtration with suction through a celite pad on a glass filter, the filtrate was washed with 15% aqueous NaOH and sat. NaCl. Organic phase was dried ($MgSO_4$), and the solvent was removed *in vacuo*. The residue was subjected to column chromatography on silica gel (hexane/ethyl acetate = 8:1, v/v) to give diol **1k** (0.82 g) in 85% yield.

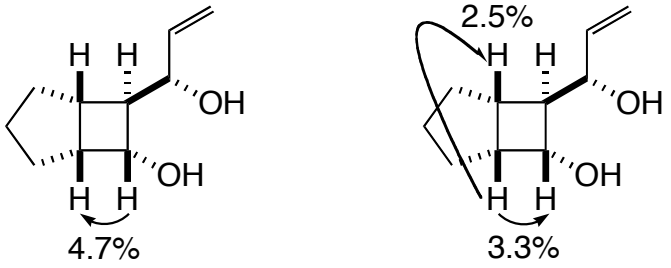
3-(1-Hydroxyallyl)-6,6-dimethylbicyclo[3.1.1]heptan-2-ol (**1d**) [8]: (single isomer): mp 88.5 ºC (dichloromethane – hexane); IR (neat) 3287 (s), 3086 (s), 2924 (s), 1466 (s), 1335 (s), 1157 (s), 1126 (s), 1080 (s), 1018 (s), 934 (s), 795 (m), 687 (s) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.70 (d, *J* = 10.0 Hz, 1 H), 1.11 (s, 3 H), 1.25 (s, 3 H), 1.37 (ddd, *J* = 2.2, 6.8, 13.4 Hz, 1 H), 1.95 (dd, *J* = 3.4, 5.9 Hz, 1 H), 2.01 (ddd, *J* = 2.4, 3.4, 13.4 Hz, 1 H), 2.05 (d, *J* = 3.4 Hz, 1 H), 2.11 (ddt, *J* = 2.2, 10.0, 3.4 Hz, 1 H), 2.23 (d, *J* = 2.7 Hz, 1 H), 2.30 (dddd, *J* = 2.4, 5.9, 6.8, 13.4 Hz, 1 H), 3.92 (dt, *J* = 2.9, 6.8 Hz, 1 H), 4.11 (dt, *J* = 6.8, 2.7 Hz, 1 H), 5.18 (dm, *J* = 10.3 Hz, 1 H), 5.30 (dm, *J* = 17.1 Hz, 1 H), 5.90 (ddd, *J* = 6.8, 10.3, 17.1 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.3, 27.7, 29.5, 30.3, 37.8, 41.5, 45.0, 48.0, 77.2, 80.2, 116.2, 139.7; HRMS calcd for $C_{12}H_{29}O_2$: 196.1463. Found *m/z* (relative intensity) 196.1449 (M^+, 2), 195 (1), 179 (16), 178 (100), 139 (49).

7-(1-Hydroxyallyl)bicyclo[3.2.0]heptan-6-ol (**1a**): (a mixture of 3 isomers in a 1 : 6 : 7 ratio): Yields: Aldol, 100%; LAH reduction, 78%; IR (neat) 3400 (s), 2930 (w), 1650 (m), 1065 (w), 985 (w), 915 (w) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, ***anti*-1a**) δ 1.36-1.49 (m, 3 H), 1.53 (dt, *J* = 5.9, 12.0 Hz, 1 H), 1.66 (dd, *J* = 5.9, 12.0 Hz, 1 H), 1.77 (dt, *J* = 12.0, 5.9 Hz, 1 H), 1.86 (dt, *J* = 4.6, 7.6 Hz, 1 H), 2.42 (m, 1 H, coalescing to t, *J* = 7.6 Hz by irradiation at 1.86), 2.53 (dt, *J* = 2.9, 7.6 Hz, 1 H), 3.35 (br s, 1 H), 3.42 (br s, 1 H), 3.98 (dd, *J* = 2.9, 7.6 Hz, 1 H), 4.42 (dd, *J* = 6.8, 7.6 Hz, 1 H), 5.13 (dm, *J* = 10.5 Hz, 1 H), 5.25 (dm, *J* = 17.2 Hz, 1 H), 5.81 (ddd, *J* = 6.8, 10.5, 17.2 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$, ***anti*-1a**) δ 25.7, 30.9, 31.4, 36.2, 46.1, 47.7, 72.2, 74.1, 115.5, 138.6; ^1H NMR (400 MHz, $CDCl_3$, ***syn*-1a**) δ 1.41-

1.55 (m, 3 H), 1.65 (ddd, *J* = 5.6, 6.3, 8.5 Hz, 1 H), 1.72 (dt, *J* = 12.6, 6.6 Hz, 1 H), 1.82 (m, 1 H), 1.97 (dd, *J* = 7.1, 13.4 Hz, 1 H), 2.14 (dt, *J* = 7.3, 5.6 Hz, 1 H), 2.39 (m, 2 H), 2.79 (dt, *J* = 7.3, 8.3 Hz, 1 H), 4.05 (dd, *J* = 6.3, 8.5 Hz, 1 H), 4.17 (dd, *J* = 6.3, 8.3 Hz, 1 H), 5.12 (dm, *J* = 10.5 Hz, 1 H), 5.25 (dm, *J* = 17.1 Hz, 1 H), 5.81 (ddd, *J* = 6.3, 10.5, 17.1 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$, ***syn*-1a**) δ 24.4, 26.2, 32.2, 35.2, 41.4, 54.2, 67.4, 76.1, 115.1, 138.7. HRMS calcd for $C_{10}H_{16}O_2$: 168.1150. Found *m/z* (relative intensity) 168.1135 (M^+, 1), 167 (2), 151 (18), 150 (100).



***anti*-1a**



***syn*-1a**

NOE Increments (%) Observed for ***anti*-1a** and ***syn*-1a**

7-[(2*E*)-1-Hydroxy-2-butenyl]bicyclo[3.2.0]heptan-6-ol (**1b**): (a mixture of 4 isomers in a 1 : 5 : 6 : 6 ratio): Yields: Aldol, 63%; LAH reduction, 93%; IR (neat) 3418 (s), 3024 (w), 2947 (s), 2862 (m), 1651 (s), 1443 (m), 1319 (m), 1250 (m), 1072 (s), 972 (s) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, ***anti*-1b**) δ 1.33-1.49 (m, 3 H), 1.54 (dq, *J* = 17.6, 6.0 Hz, 1 H), 1.66 (dd, *J* = 6.0, 12.2 Hz, 1 H), 1.71 (dd, *J* = 1.0, 6.6 Hz, 3 H), 1.77 (dt, *J* = 12.2, 6.0 Hz, 1 H), 1.85 (dddd, *J* = 1.0, 4.6, 7.6, 8.5 Hz, 1 H), 2.38 (dt, *J* = 4.6, 7.3 Hz, 1 H), 2.48 (dt, *J* = 3.2, 7.3 Hz, 1 H), 2.68 (m, 1 H), 3.98 (dd, *J* = 3.2, 7.3 Hz, 1 H), 4.38 (dd, *J* = 7.3, 8.5 Hz, 1 H), 5.46 (dd, *J*

= 7.3, 15.4 Hz, 1 H), 5.72 (ddq, *J* = 1.0, 15.4, 6.6 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$, ***anti*-1b**) δ 17.8, 25.7, 30.9, 31.4, 36.2, 46.2, 47.8, 72.4, 74.1, 127.9, 131.7; ^{1}H NMR (400 MHz, $CDCl_3$, ***syn*-1b**) δ 1.38-1.58 (m, 3 H), 1.63 (dt, *J* = 8.5, 6.6 Hz, 1 H), 1.70 (dd, *J* = 1.6, 6.6 Hz, 1 H), 1.71 (m, 1 H), 1.81 (m, 1 H), 1.95 (m, 2 H), 1.96 (dd, *J* = 7.3, 13.4 Hz, 1H), 2.10 (q, *J* = 6.6 Hz, 1 H), 2.77 (dt, *J* = 6.6, 7.8 Hz, 1 H), 3.99 (dd, *J* = 7.6, 8.5 Hz, 1 H), 4.15 (dd, *J* = 6.6, 7.8 Hz, 1 H), 5.43 (ddq, *J* = 7.6, 15.4, 1.6 Hz, 1 H), 5.69 (dq, *J* = 15.4, 6.6 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$, ***syn*-1b**) δ 17.7, 24.4, 26.2, 32.2, 35.2, 41.3, 54.4, 67.5, 75.9, 127.4, 131.7; ^{1}H NMR (400 MHz, $CDCl_3$, other stereoisomer **1b**) δ 1.36-1.63 (m, 4 H), 1.67 (dd, *J* = 5.1, 12.2 Hz, 1 H), 1.71 (d, *J* = 6.6 Hz, 3 H), 1.77 (dq, *J* = 12.2, 6.1 Hz, 1 H), 1.95 (ddd, *J* = 3.3, 5.2, 7.8 Hz, 1 H), 2.44 (br s, 1 H), 2.48 (dt, *J* = 3.7, 7.8 Hz, 1 H), 2.81 (*J* = 7.8, 5.1 Hz, 1 H), 3.19 (br d, *J* = 7.8 Hz, 1 H), 3.91 (m, 1 H), 4.50 (m, 1 H), 5.53 (dd, *J* = 6.6, 15.4 Hz, 1 H), 5.70 (dq, *J* = 15.4, 6.6 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$, other stereoisomer **1b**) δ 17.8, 25.7, 31.2, 31.8, 33.5, 47.9, 49.2, 71.5, 73.5, 126.8, 131.2; HRMS calcd for $C_{11}H_{18}O_2$: 182.1307. Found *m/z* (relative intensity) 182.1330 (M^+, 1), 165 (13), 164 (100).

7-(1-Hydroxy-2-methylallyl)bicyclo[3.2.0]heptan-6-ol (**1c**): (a mixture of 2 isomers in a 1 : 1 ratio): Yields: Aldol, 30%; LAH reduction, 63%; IR (neat) 3356 (s), 3078 (m), 2939 (s), 2855 (s), 1651 (m), 1443 (m), 1327 (m), 1072 (m), 964 (w), 903 (w) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, ***anti*-1c**) δ 1.38-1.48 (m, 3 H), 1.57 (m, 1 H), 1.68 (dd, *J* = 5.4, 12.2 Hz, 1 H), 1.73 (s, 3 H), 1.79 (m, 1 H), 2.01 (dddd, *J* = 1.2, 4.6, 7.3, 9.7 Hz, 1 H), 2.35 (br dq, *J* = 7.8, 4.6 Hz, 1 H), 2.43 (d, *J* = 3.5 Hz, 1 H), 2.53 (dt, *J* = 3.2, 7.8 Hz, 1 H), 2.55 (d, *J* = 3.2 Hz, 1 H), 4.02 (dt, *J* = 7.3, 3.2 Hz, 1 H), 4.43 (dd, *J* = 3.5, 9.7 Hz, 1 H), 4.90 (s, 1 H), 4.97 (s, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$, ***anti*-1c**) δ 17.7, 25.7, 30.8, 31.5, 36.4, 45.4, 45.9, 72.3, 76.8, 112.9, 144.9; ^{1}H NMR (400 MHz, $CDCl_3$, ***syn*-1c**) δ 1.38-1.52 (m, 3 H), 1.68-1.84 (m, 2 H), 1.72 (s, 3 H), 1.76 (ddd, *J* = 5.9, 6.6, 9.3 Hz, 1 H), 1.95 (br s, 1 H), 1.97 (dd, *J* = 7.1, 13.7 Hz, 1 H), 2.06 (m, 1 H), 2.11 (br q, *J* = 6.6 Hz, 1 H), 2.79 (dt, *J* = 6.6, 7.8 Hz, 1 H), 4.01 (d, *J* = 9.3 Hz, 1 H),

4.19 (dt, *J* = 7.8, 5.9 Hz, 1 H), 4.84 (s, 1 H), 4.95 (s, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$, ***syn*-1c**) δ 17.7, 24.4, 26.2, 32.1, 35.6, 41.4, 52.3, 67.8, 79.3, 111.8, 145.7; HRMS calcd for $C_{11}H_{18}O_2$: 182.1307. Found *m/z* (relative intensity) 182.1331 (M^+, 1), 165 (16), 164 (100).

3-(1-Hydroxyallyl)bicyclo[2.2.1]heptan-2-ol (**1e**): (a mixture of 3 isomers in a 1 : 6 : 19 ratio): Yields: Aldol, 86%; LAH reduction, 88%; IR (neat) 3371 (s), 2955 (s), 2878 (s), 1427 (m), 1304 (m), 1126 (m), 1042 (s), 995 (s), 926 (s), 764 (w) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, major isomer) δ 1.09 (br dt, *J* = 9.8, 2.0 Hz, 1 H), 1.19 (dq, *J* = 10.3, 2.0 Hz, 1 H), 1.32 (m, 1 H), 1.40 (ddt, *J* = 1.5, 11.5, 4.0 Hz, 1 H), 1.47 (br d, *J* = 10.3 Hz, 1 H), 1.59 (dt, *J* = 11.5, 4.6 Hz, 1 H), 1.73 (br s, 1 H), 1.87 (m, 1 H), 1.98 (br s, 2 H), 2.31 (br s, 1 H), 3.80 (br t, *J* = 7.3 Hz, 1 H), 4.10 (br s, 1 H), 5.14 (ddd, *J* = 1.0, 1.5, 10.3 Hz, 1 H), 5.21 (dt, *J* = 17.3, 1.5 Hz, 1 H), 5.86 (ddd, *J* = 7.3, 10.3, 17.3 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$, major isomer) δ 19.6, 30.6, 35.1, 39.5, 42.5, 57.0, 76.6, 77.0, 115.7, 140.3; HRMS calcd for $C_{10}H_{16}O_2$: 168.1150. Found *m/z* (relative intensity) 168.1145 (M^+, 5), 167 (1), 151 (12), 150 (100).

3-(1-Hydroxyallyl)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-ol (**1g**): (a mixture of 2 isomers in a 1 : 3 ratio): Yields: Aldol, 96%; LAH reduction, 83%; mp 91.0 – 92.0 ºC (dichloromethane – hexane); IR (KBr) 3352 (s), 3084 (w), 3040 (w), 2937 (s), 1435 (s), 1367 (s), 1288 (s), 1271 (s), 1119 (s), 1051 (s), 926 (s), 793 (w), 712 (m) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, major isomer) δ 0.80 (s, 3 H), 0.95 (s, 3 H), 0.99 (ddd, *J* = 4.0, 9.1, 11.7 Hz, 1 H), 1.06 (ddd, *J* = 4.0, 9.1, 11.7 Hz, 1 H), 1.19 (s, 3 H), 1.48 (dt, *J* = 11.7, 4.0 Hz, 1 H), 1.57 (d, *J* = 4.0 Hz, 1 H), 1.70 (tt, *J* = 4.0, 11.7 Hz, 1 H), 1.79 (dd, *J* = 7.8, 11.0 Hz, 1 H), 2.58 (d, *J* = 2.0 Hz, 1 H), 2.83 (br s, 1 H), 3.90 (dd, *J* = 2.0, 7.8 Hz, 1 H), 4.54 (dd, *J* = 7.1, 11.0 Hz, 1 H), 5.17 (dm, *J* = 10.3 Hz, 1 H), 5.24 (dm, *J* = 17.3 Hz, 1 H), 5.86 (ddd, *J* = 7.1, 10.3, 17.3 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$, major isomer) δ 11.4, 21.6, 22.0, 29.7, 33.4, 47.0, 47.5, 49.6, 56.2, 74.3, 82.1, 116.1, 140.2; HRMS calcd for $C_{13}H_{22}O_2$: 210.1620. Found *m/z* (relative

intensity) 210.1595 (M^+, 27), 209 (3), 208 (10), 193 (19), 192 (100).

3-(1-Hydroxy-2-methylallyl)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-ol (**1h**): (a mixture of 2 isomers in a 1 : 4 ratio): Yields: Aldol, 100%; LAH reduction, 93%; IR (neat) 3326 (s), 2951 (s), 2885 (s), 1452 (m), 1371 (m), 1288 (m), 1103 (s), 1053 (s), 1016 (s), 959 (s), 905 (s) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, major isomer) δ 0.78 (s, 3 H), 0.96 (s, 3 H), 1.00 (ddd, *J* = 3.3, 9.3, 12.7 Hz, 1 H), 1.08 (ddd, *J* = 4.6, 9.3, 12.7 Hz, 1 H), 1.18 (s, 3 H), 1.45 (d, *J* = 4.6 Hz, 1 H), 1.48 (dt, *J* = 3.3, 12.7 Hz, 1 H), 1.69 (dtt, *J* = 1.0, 12.7, 4.6 Hz, 1 H), 1.75 (dd, *J* = 1.0, 1.5 Hz, 1 H), 1.93 (dd, *J* = 7.8, 11.2 Hz, 1 H), 2.50 (d, *J* = 2.2 Hz, 1 H), 2.49 (d, *J* = 2.2 Hz, 1 H), 3.90 (dd, *J* = 2.2, 7.8 Hz, 1 H), 4.59 (dd, *J* = 2.2, 11.2 Hz, 1 H), 4.91 (q, *J* = 1.5 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$, major isomer) δ 11.4, 16.8, 21.6, 22.0, 29.9, 33.6, 47.0, 47.6, 49.6, 53.5, 81.9, 113.9, 146.0; HRMS calcd for $C_{14}H_{24}O_2$: 224.1776. Found *m/z* (relative intensity) 225 (M^++1, 1), 224.1787 (M^+, 6), 207 (16), 206 (100).

3-[(2*E*)-1-hydroxy-3-phenylallyl]-1,7,7-trimethylbicyclo[2.2.1]heptan-2-ol (**1i**): (a mixture of 3 isomers in a 1 : 5 : 8 ratio): Yields: Aldol, 100%; LAH reduction, 95%; IR (neat) 3402 (s), 2955 (s), 1651 (w), 1450 (m), 1103 (m), 1042 (m), 964 (m), 748 (s), 694 (s) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, major isomer) δ 0.80 (s, 3 H), 0.96 (s, 3 H), 1.01 (ddd, *J* = 3.4, 9.0, 11.7 Hz, 1 H), 1.08 (ddd, *J* = 4.2, 9.0, 11.7 Hz, 1 H), 1.25 (s, 3 H), 1.52 (dt, *J* = 3.4, 11.7 Hz, 1 H), 1.60 (d, *J* = 4.2 Hz, 1 H), 1.69 (tt, *J* = 4.2, 11.7 Hz, 1 H), 1.90 (dd, *J* = 7.8, 11.7 Hz, 1 H), 2.59 (d, *J* = 2.2 Hz, 1 H), 2.90 (s, 1 H), 3.93 (dd, *J* = 2.2, 7.8 Hz, 1H), 4.73 (ddd, *J* = 1.7, 7.8, 11.7 Hz, 1 H), 6.21 (dd, *J* = 7.8, 15.6 Hz, 1 H), 6.58 (d, *J* = 15.6 Hz, 1 H), 7.25 (t, *J* = 7.4 Hz, 1 H), 7.31 (t, *J* = 7.4 Hz, 2 H), 7.38 (d, *J* = 7.4 Hz, 1 H), 7.41 (d, *J* = 7.4 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$, major isomer) δ 11.4, 21.7, 22.0, 29.8, 33.4, 47.0, 47.6, 49.6, 56.6, 74.0, 82.1, 126.4, 127.6, 128.4, 131.4, 131.5, 136.6; HRMS calcd for $C_{19}H_{26}O_2$: 286.1933. Found *m/z* (relative intensity) 287 (M^++1, 26), 286.1921 (M^+, 100), 285 (7), 269 (71).

3-[(2*E*)-1-Hydroxy-2-methyl-2-butenyl]-1,7,7-trimethylbicyclo[2.2.1]heptan-2-ol (**1j**): Yields: Aldol, 100%; LAH reduction, 95%; IR (KBr) 3395 (s), 2947 (s), 2878 (s), 1443 (s), 1335 (s), 1242 (s), 1103 (s), 1034 (s), 957 (s), 856 (m), 818 (s), 710 (m) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.77 (s, 3 H), 0.95 (s, 3 H), 0.97 (ddd, *J* = 3.3, 9.3, 12.8 Hz, 1 H), 1.08 (ddd, *J* = 4.2, 9.3, 12.8 Hz, 1 H), 1.17 (s, 3 H), 1.37 (d, *J* = 4.2 Hz, 1 H), 1.47 (dt, *J* = 3.3, 12.8 Hz, 1 H), 1.62 (s, 3 H), 1.64 (d, *J* = 6.6 Hz, 3 H), 1.68 (tt, *J* = 4.2, 12.8 Hz, 1 H), 1.95 (dd, *J* = 7.8, 11.2 Hz, 1 H), 2.32 (d, *J* = 2.0 Hz, 1 H), 2.61 (d, *J* = 2.0 Hz, 1 H), 3.88 (dd, *J* = 2.0, 7.8 Hz, 1 H), 4.49 (dd, *J* = 2.0, 11.2 Hz, 1 H), 5.49 (q, *J* = 6.6 Hz, 1 H) ^{13}C NMR (100 MHz, $CDCl_3$) δ 10.7, 11.5, 13.1, 21.6, 22.1, 30.0, 33.6, 46.9, 47.6, 49.6, 53.3, 78.9, 81.9, 123.3, 136.9; HRMS calcd for $C_{15}H_{26}O_2$: 238.1933. Found *m/z* (relative intensity) 239 (M^++1, 10), 238.1943 (M^+, 12), 221 (18), 220 (100).

3-(1-Hydroxyallyl)-1,2,7,7-tetramethylbicyclo[2.2.1]heptan-2-ol (**1k**): (a mixture of 2 isomers in a 1 : 7 ratio): Yields: Aldol, 100%; MeLi, 22%; IR (neat) 3333 (s), 2955 (s), 1736 (s), 1450 (s), 1381 (s), 1119 (s), 1042 (s), 995 (s), 918 (s), 826 (w), 694 (m) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, major isomer) δ 0.82 (s, 3 H), 0.88 (s, 3 H), 1.01 (ddd, *J* = 4.5, 9.0, 12.2 Hz, 1 H), 1.26 (s, 3 H), 1.35 (s, 3 H), 1.37 (dd, *J* = 4.5, 13.4 Hz, 1 H), 1.47 (ddd, *J* = 4.5, 9.0, 13.4 Hz, 1 H), 1.47 (d, *J* = 10.7 Hz, 1 H), 1.55 (d, *J* = 4.5 Hz, 1 H), 1.74 (tt, *J* = 4.5, 12.2 Hz, 1 H), 2.23 (s, 1 H), 2.55 (br s, 1 H), 4.54 (dd, *J* = 7.1, 10.7 Hz, 1 H), 5.15 (dm, *J* = 10.3 Hz, 1 H), 5.22 (dm, *J* = 17.3 Hz, 1 H), 5.85 (ddd, *J* = 7.1, 10.3, 17.3 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$, major isomer) δ 9.7, 22.7, 22.8, 29.2, 29.7, 31.2, 47.5, 49.4, 52.7, 62.7, 75.2, 82.6, 115.9, 140.3; HRMS calcd for $C_{14}H_{24}O_2$: 224.1776. Found *m/z* (relative intensity) 225 (M^++1, 15), 224.1763 (M^+, 100), 209 (11), 206 (87).

2,3-Dihydro-2-[(2*E*)-1-hydroxy-2-butenyl]-1*H*-inden-1-ol (**1m**): (a mixture of 3 isomers in a 1.8 : 1.5 : 1 ratio): Yields: Aldol, 96%; LAH reduction, 100%; IR (neat) 3379 (s), 3032 (m),

2916 (s), 2855 (m), 1443 (s), 1312 (m), 1211 (m), 1173 (w), 1057 (s), 972 (s), 748 (s) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, major isomer) δ 1.73 (dd, *J* = 1.5, 6.3 Hz, 1 H), 2.45 (m, 1 H), 2.48 (dd, *J* = 9.5, 15.6 Hz, 1 H), 2.88 (dd, *J* = 8.3, 15.6 Hz, 1 H), 4.21 (t, *J* = 7.6 Hz, 1 H), 5.18 (d, *J* = 7.8 Hz, 1 H), 5.56 (ddq, *J* = 7.6, 15.1, 1.5 Hz, 1 H), 5.75 (dq, *J* = 15.1, 6.3 Hz, 1 H), 7.14-7.27 (m, 3 H), 7.36 (m, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$, a mixture of 3 isomers) δ 17.7, 32.8, 56.0, 77.4, 79.9, 123.6, 124.4, 126.6, 127.8, 128.7, 132.7, 140.5, 144.1; HRMS calcd for $C_{13}H_{16}O_2$: 204.1150. Found *m/z* (relative intensity) 205 (M^++1, 1), 204.1154 (M^+, 7), 187 (14), 186 (100).

2-(1-Hydroxyallyl)-4-phenylcyclohexanol (**1r**): (a mixture of 4-isomers, the ratio was not determined): Yields: Aldol, 70%; LAH reduction, 100%; IR (KBr) 3275 (s), 2930 (s), 1498 (m), 1450 (s), 1349 (m), 1150 (m), 1085 (s), 1020 (s), 925 (s), 765 (s), 700 (s) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, major isomer) δ 1.11 (dt, *J* = 13.4, 12.2 Hz, 1 H), 1.53 (m, 2 H), 1.64 (ddt, *J* = 3.4, 5.9, 9.3 Hz, 1 H), 1.82 (dq, *J* = 13.4, 3.4 Hz, 1 H), 1.90 (m, 1 H), 2.11 (m, 1 H), 2.56 (tt, *J* = 3.4, 12.2 Hz, 1 H), 3.04 (m, 1 H), 3.72 (dt, *J* = 4.6, 9.3 Hz, 1 H), 3.76 (m, 1 H), 4.12 (dd, *J* = 5.9, 6.3 Hz, 1 H), 5.14 (dm, *J* = 10.3 Hz, 1 H), 5.21 (dm, *J* = 17.1 Hz, 1 H), 5.84 (ddd, *J* = 6.3, 10.3, 17.1 Hz, 1 H), 7.17 (d, *J* = 6.8 Hz, 2 H), 7.27 (d, *J* = 6.8 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$, major isomer) δ 31.9, 35.2, 35.4, 43.2, 48.5, 75.2, 79.7, 117.1, 126.1, 126.6, 128.3, 139.0, 146.1; HRMS calcd for $C_{15}H_{20}O_2$: 232.1463. Found *m/z* (relative intensity) 233 (M^++1, 2), 232.1454 (M^+, 12), 215 (18), 214 (100).

2-(1-Hydroxyallyl)cycloheptanol (**1s**): (a mixture of 4 isomers, the ratio was not determined): Yields: Aldol, 80%; LAH reduction, 92%; IR (neat) 3356 (s), 2924 (s), 2862 (s), 1450 (s), 1296 (m), 1134 (m), 1057 (m), 995 (s), 926 (s), 725 (w) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, major isomer) δ 1.08-1.88 (m, 11 H), 2.60 (m, 1 H), 2.92 (m, 1 H), 4.25 (m, 1 H), 4.43 (m, 1 H), 5.17 (dt, *J* = 10.7, 1.5 Hz, 1 H), 5.27 (dt, *J* = 17.1, 1.7 Hz, 1 H), 5.89 (ddd, *J* = 4.6,

10.7, 17.1 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$, a mixture of 4 isomers) δ 19.2, 21.6, 21.9, 22.7, 25.4, 26.0, 26.4, 27.2, 27.3, 27.7, 28.0, 28.3, 28.4, 28.8, 29.7, 35.7, 36.3, 36.8, 37.1, 48.0, 48.1, 50.8, 51,6, 70.4, 73.3, 74.8, 75.8, 78.9, 114.1, 115.2, 115.7, 117.2, 137.8, 139.7, 140.0, 140.3; HRMS calcd for $C_{10}H_{18}O_2$: 170.1307. Found *m/z* (relative intensity) 171 (M^++1, 56), 170.1335 (M^+, 22), 169 (100).

2-(1-Hydroxyallyl)cyclooctanol (**1t**): (a mixture of 4 isomers, the ratio was not determined): Yields: Aldol, 100%; LAH reduction, 93%; IR (neat) 3248 (s), 2932 (s), 1643 (s), 1450 (m), 1304 (m), 1126 (m), 988 (m), 926 (m) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, major isomer) δ 1.14-2.00 (m, 13 H), 2.70 (m, 1 H), 3.07 (m, 1 H), 4.16 (m, 1 H), 4.45 (m, 1 H), 5.19 (dt, *J* = 10.6, 1.7 Hz, 1H), 5.34 (dt, *J* = 17.1, 1.7 Hz, 1 H), 5.87 (ddd, *J* = 4.6, 10.6, 17.1 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$, a mixture of 4 isomers) δ 18.5, 21.1, 21.7, 22.0, 23.8, 24.4, 24.7, 25.0, 25.1, 25.4, 25.8, 26.2, 26.6, 27.1, 27.3, 27.4, 27.5, 27.6, 28.4, 28.6, 32.6, 32.8, 33.0, 33.4, 44.3, 44.4, 46.6, 47.8, 70.6, 73.2, 75.9, 77.7, 77.8, 79.3, 114.4, 115.2, 115.6, 117.0, 137.8, 139.6, 139.8, 140.2; HRMS calcd for $C_{11}H_{20}O_2$: 184.1463. Found *m/z* (relative intensity) 185 (M^++1, 1), 184.1463 (M^+, 1), 183 (2), 167 (13), 166 (100).

2-(1-Hydroxyallyl)cyclodecanol (**1u**): (a mixture of 4 isomers, the ratio was not determined): Yields: Aldol, 94%; LAH reduction, 96%; IR (neat) 3379 (s), 2932 (s), 1643 (m), 1443 (m), 1242 (w), 1111 (w), 1042 (w), 995 (m), 918 (w) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, major isomer) δ 1.23-2.18 (m, 17 H), 2.92 (m, 1 H), 3.28 (m, 1 H), 4.26 (m, 1 H), 4.46 (m, 1 H), 5.11 (dt, *J* = 10.6, 1.7 Hz, 1 H), 5.33 (dt, *J* = 17.1, 1.6 Hz, 1 H), 5.91 (ddd, *J* = 5.3, 10.6, 17.1 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$, a mixture of 4 isomers) δ 17.3, 20.8, 21.5, 21.9, 22.1, 22.4, 24.0, 24.2, 24.3, 24.7, 25.0, 25.1, 25.3, 25.4, 25.5, 25.6, 25.7, 26.0, 26.1, 26.8, 31.7, 32.3, 33.1, 42.6, 43.0, 45.1, 46.3, 71.9, 73.1, 75.1, 75.4, 75.7, 78.0, 79.4, 113.8, 114.9, 115.7, 116.2, 138.1, 139.9, 140.0, 140.5; HRMS calcd for $C_{13}H_{24}O_2$: 212.1776. Found *m/z* (relative

intensity) 213 (M^++1, 1), 212.1754 (M^+, 3), 211 (2), 195 (15), 194 (100).

2-(1-Hydroxyallyl)cyclododecanol (**1v**): (a mixture of 3 isomers, the ratio was not determined): Yields: Aldol, 100%; LAH reduction, 97%; IR (neat) 3564 (s), 2939 (s), 2862 (m), 1643 (s), 1466 (m), 1312 (w), 1003 (w), 918 (w) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, major isomer) δ 1.18- 1.55 (m, 17 H), 2.73 (m, 1 H), 4.01 (m, 1 H), 4.29 (m, 1 H), 5.20 (dt, *J* = 10.5, 1.5 Hz, 1 H), 5.31 (dt, *J* = 17.2, 1.5 Hz, 1 H), 5.90 (ddd, *J* = 5.7, 10.5, 17.2 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$, a mixture of 3 isomers) δ 20.1, 20.8, 21.0, 21.6, 21.7, 21.8, 22.0, 22.2, 22.5, 22.6, 22.7, 23.0, 23.1, 23.3, 23.4, 23.5, 23.6, 23.8, 23.9, 24.0, 24.1, 24.2, 24.3, 24.4, 24.5, 24.6, 24.9, 25.4, 25.5, 25.6, 26.2, 26.4, 27.2, 30.1, 32.3, 32.5, 40.6, 41.9, 43.0, 56.1, 57.3, 69.2, 70.7, 71.7, 72.7, 73.4, 73.8, 75.0, 115.4, 115.5, 116.0, 138.2, 138.4, 138.7, 140.5; HRMS calcd for $C_{15}H_{28}O_2$: 240.2089. Found *m/z* (relative intensity) 240.2095 (M^+, 4), 239 (4), 223 (17), 222 (100), 213 (2), 183 (11).

2-[(2*E*)-1-hydroxy-2-butenyl]cyclododecanol (**1w**): (a mixture of 4 isomers, the ratio was not determined): Yields: Aldol, 100%; LAH reduction, 100%; IR (neat) 3333, (s), 2932 (s), 2862 (s), 1450 (m), 1335 (w), 1157 (w), 1011 (w), 972 (w) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, major isomer was assigned) δ 1.12-1.54 (m, 14 H), 1.55-1.68 (m, 2 H), 1.73 (d, *J* = 6.3 Hz, 3 H), 1.80 (m, 1 H), 2.56 (m, 1 H), 2.99 (m, 1 H), 4.02 (br t, *J* = 5.4 Hz, 1 H), 4.19 (t, *J* = 6.8 Hz, 1 H), 5.53 (ddd, *J* = 1.5, 6.8, 15.1 Hz, 1 H), 5.70 (dq, *J* = 15.1, 6.3 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$, a mixture of 4 isomers) δ 17.6, 17.7, 17.8, 21.5, 21.6, 21.8, 21.9, 22.1, 22.8, 23.3, 23.4, 23.5, 23.7, 23.8, 24.0, 24.1, 24.4, 24.8, 25.1, 26.0, 26.1, 26.2, 29.5, 32.1, 33.4, 42.1, 43.0, 44.2, 45.0, 70.6, 71.8, 73.1, 73.8, 75.2, 75.5, 77.2, 77.5, 125.7, 127.6, 127.7, 131.1, 133.2, 133.3, 133.4; HRMS calcd for $C_{16}H_{30}O_2$: 254.2246. Found *m/z* (relative intensity) 255 (M^++1, 18), 254.2236 (M^+, 100), 253 (28).

2-(1-hydroxy-2-methylallyl)cyclododecanol (**1x**): (a mixture of 4 isomers, the ratio was not determined): Yields: Aldol, 100%; LAH reduction, 81%; IR (neat) 3379 (s), 2931 (s), 2862 (s), 1651 (m), 1450 (s), 1157 (m), 1096 (s), 1026 (s), 903 (s), 725 (m) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, a major isomer was assigned) δ 1.12-1.48 (m, 18 H), 1.53 (m, 1 H), 1.70 (s, 3 H), 1.73 (s, 3 H), 2.81 (m, 1 H), 3.08 (m, 1 H), 3.95 (m, 1 H), 4.21 (d, *J* = 8.9 Hz, 1 H), 4.97 (s, 1 H), 5.08 (s, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$, a mixture of 4 isomers) δ 16.8, 16.9, 18.4, 20.0, 21.0, 21.1, 21.5, 21.6, 21.8, 21.9, 22.0, 22.1, 22.5, 22.6, 23.1, 23.2, 23.4, 23.7, 23.9, 24.0, 24.5, 24.8, 25.3, 25.4, 25.7, 26.1, 26.2, 26.3, 26.6, 29.8, 32.4, 33.3, 33.6, 37.7, 38.8, 39.7, 41.7, 70.1, 70.3, 73.2, 73.4, 77.0, 77.6, 79.8, 80.5, 109.8, 110.3, 111.8, 113.4, 145.4, 146.1, 146.2, 146.5; HRMS calcd for $C_{16}H_{30}O_2$: 254.2246. Found *m/z* (relative intensity) 255 (M^++1, 1), 254.2240 (M^+, 3), 253 (1), 237 (19), 236 (100).

Preparation of *B*-Ph-9-BBN. [4] Into a nitrogen purged Schlenk flask, were introduced by dry pentane (5 mL) and *B*-methoxy-9-BBN (5 mL, 1.0 M hexanes solution, 5 mmol) via syringe. The mixture was cooled at –78 ºC. PhLi (5 mL, 1.0 M cyclohexane-diethyl ether solution, 5 mmol) was added slowly via syringe. A white precipitate was formed immediately. The mixture was stirred at –78 ºC for 15 minutes and then allowed to warm to room temperature and was stirred for 12 hours. The supernatant solution was used as 0.3 M *B*-Ph-9-BBN.

General Procedure for Palladium Catalyzed C-C Bond Cleavage Reaction of 4-Penten-1,3-diol (Table 2, Run 4). Into a flask containing $Pd(PPh_3)_4$ (29 mg, 0.025 mmol) purged with N_2 were successively added dry toluene (2.5 mL), 1,3-diol **1d** (98.1 mg, 0.5 mmol), and *B*-Ph-9-BBN (0.8 mL, 0.3 M solution , 0.25 mmol) via syringe at room temperature. The homogeneous solution was stirred at 50 ºC for 24 hours under N_2. The mixture was diluted with ethyl acetate and washed with brine, and dried ($MgSO_4$), and concentrated *in vacuo*. The residue was purification by column chromatography over silica gel (hexane/ethyl acetate =

64:1, v/v) to give **2d** in 92% yield (80.2 mg). R_f (**2d**) = 0.83 (hexane/ethyl acetate = 2:1, v/v).

2,2-Dimethyl-3-(2,4-pentadienyl)cyclobutanecarbaldehyde (**2d**) (a mixture of *E*- and *Z*-isomers in a ratio of 1 : 1): IR (neat) 3086 (w), 3007 (m), 2955 (s), 2712 (m), 1715 (s), 1651 (m), 1603 (w), 1464 (s), 1369 (s), 1157 (m), 1005 (s), 901 (s) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, (***E*)-2d**) δ 1.03 (s, 3 H), 1.28 (s, 3 H), 1.97 (dt, *J* = 2.0, 8.3 Hz, 2 H), 2.01-2.10 (m, 2 H), 2.14 (m, 1 H), 2.75 (dt, *J* = 2.0, 8.8 Hz, 1 H), 4.96 (dm, *J* = 10.5 Hz, 1 H), 5.09 (dm, *J* = 16.8 Hz, 1 H), 5.57 (dt, *J* = 15.1, 7.8 Hz, 1 H), 6.05 (ddm, *J* = 10.5, 15.1 Hz, 1 H), 6.28 (dt, *J* = 16.8, 10.5 Hz, 1 H), 9.71 (dd, *J* = 1.2, 2.0 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$, (***E*)-2d**) δ 18.0, 22.4, 31.1, 33.3, 42.3, 53.2, 114.9, 131.7, 132.4, 136.9, 203.4; ^1H NMR (400 MHz, $CDCl_3$, (***Z*)-2d**) δ 1.04 (s, 3 H), 1.29 (s, 3 H), 2.23 (m, 1 H), 5.11 (dm, *J* = 10.0 Hz, 1 H), 5.19 (dm, *J* = 16.8 Hz, 1 H), 5.33 (br dt, *J* = 11.0 Hz, 7.8 Hz, 1 H), 5.99 (tm, *J* = 11.0 Hz, 1 H), 6.63 (dddd, *J* = 1.0, 10.0, 11.0, 16.8 Hz, 1 H), 9.85 (d, *J* = 2.0 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$, (***Z*)-2d**) δ 22.0, 22.6, 31.6, 33.8, 42.6, 53.1, 117.2, 129.8, 131.9, 136.9, 203.9; HRMS calcd for $C_{12}H_{18}O$: 178.1358. Found *m/z* (relative intensity) 179 (M^++1, 14), 178.1339 (M^+, 100), 163 (5).

Spectral data of ω-dienyl aldehyde **2g**, **2h**, **2*l***, **2m**, **2n**, **2p**, **2t**, **2u**, and **2v** were reported previously from our laboratory. [2]

2-(1,3-Butadienyl)cyclopentanecarbaldehyde (**2a**): (mixture of *E*- and *Z*- isomers in a ratio of 11 : 1): IR (neat) 2955 (s), 2870 (m), 1720 (s), 1003 (m), 903 (w) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, (***E*)-2a**) δ 1.41-2.09 (m, 6 H), 2.54 (dq, *J* = 2.7, 8.9 Hz, 1 H), 2.78 (dq, *J* = 7.8, 8.9 Hz, 1 H), 5.00 (dm, *J* = 10.3 Hz, 1 H), 5.13 (dm, *J* = 17.1 Hz, 1 H), 5.67 (dd, *J* = 7.8, 15.6 Hz, 1 H), 6.08 (dd, *J* = 10.3, 15.6 Hz, 1 H), 6.28 (dt, *J* = 17.1, 10.3 Hz, 1 H), 9.61 (d, *J* = 2.7 Hz, 1

H); ^{13}C NMR (100 MHz, $CDCl_3$, **(*E*)-2a**) δ 24.7, 26.2, 33.4, 57.8, 115.9, 130.8, 136.2, 136.5, 202.6; ^{1}H NMR (400 MHz, $CDCl_3$, epimer of **(*E*)-2a**) δ 2.88 (ddt, *J* = 2.7, 6.3, 8.5 Hz, 1 H), 2.98 (dq, *J* = 6.3, 8.3 Hz, 1 H), 5.01 (dm, *J* = 10.3 Hz, 1 H), 5.21 (dm, *J* = 16.8 Hz, 1 H), 5.71 (dd, *J* = 8.3, 15.9 Hz, 1 H), 6.13 (dd, *J* = 10.3, 15.9 Hz, 1 H), 6.23 (dt, *J* = 16.8, 10.3 Hz, 1 H), 9.66 (d, *J* = 2.7 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$, epimer of **(*E*)-2a**) δ 24.1, 25.0, 32.3, 45.8, 55.7, 116.2, 131.9, 133.5, 136.5, 204.2; ^{1}H NMR (400 MHz, $CDCl_3$, **(*Z*)-2a**) δ 2.52 (dq, *J* = 2.7 , 8.9 Hz, 1 H), 3.21 (dq, *J* = 11.0, 8.9 Hz, 1 H), 5.16 (dm, *J* = 11.0 Hz, 1 H), 5.21 (dm, *J* = 16.8 Hz, 1 H), 5.38 (br t, *J* = 11.0 Hz, 1 H), 6.00 (t, *J* = 11.0 Hz, 1 H), 6.63 (dtm, *J* = 16.8, 11.0 Hz, 1 H), 9.62 (d, *J* = 2.7 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$, **(Z)-2a**) δ 24.2, 26.2, 34.1, 39.8, 58.9, 118.0, 131.8, 134.3, 136.4 202.6; HRMS calcd for $C_{10}H_{14}O$: 150.1045. Found *m/z* (relative intensity) 151 (M^++1, 11), 150.1039 (M^+, 100), 149 (9).

2-[(1*E*)-1,3-Pentadienyl]cyclopentanecarbaldehyde (**2b**): (a mixture of *E*,*E*- and *Z*,*E*-isomers in a ratio of 2 : 1): IR (neat) 3425 (m), 3017 (s), 2955 (s), 2870 (s), 2816 (m), 2716 (m), 1720 (s), 1450 (m), 988 (s) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, **(*E*,*E*)-2b**) δ 1.46 (m, 1 H), 1.54-1.70 (m, 2 H), 1.73 (d, *J* = 6.8 Hz, 3 H), 1.75 (m, 1 H), 1.82-1.98 (m, 2 H), 2.52 (dq, *J* = 2.7, 8.5 Hz, 1 H), 2.73 (dq, *J* = 7.8, 8.5 Hz, 1 H), 5.11 (dd, *J* = 7.8, 14.4 Hz, 1 H), 5.61 (dq, *J* = 14.4, 6.8 Hz, 1 H), 5.95 (dd, *J* = 10.3, 14.4 Hz, 1 H), 6.01 (dd, *J* = 10.3, 14.4 Hz, 1 H), 9.60 (d, *J* = 2.7 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$, **(*E*,*E*)-2b**) δ 18.0, 24.7, 33.6, 40.0, 44.3, 58.0, 128.2, 130.3, 131.0, 132.8, 203.1; ^{1}H NMR (400 MHz, $CDCl_3$, **(*Z*,*E*)-2b**) δ 1.77 (d, *J* = 6.8 Hz, 1 H), 2.50 (dq, *J* = 2.4, 8.3 Hz, 1 H), 3.16 (dq, *J* = 10.0, 8.3 Hz, 1 H), 5.20 (t, *J* = 10.0 Hz, 1 H), 5.70 (dq, *J* = 14.9, 6.8 Hz, 1 H), 6.22 (ddm, *J* = 10.0, 11.0 Hz, 1 H), 9.62 (d, *J* = 2.4 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$, **(*Z*,*E*)-2b**) δ 18.3, 24.9, 34.2, 40.7, 45.9, 59.0, 126.5, 129.1, 130.4, 131.1, 203.0; ^{1}H NMR (400 MHz, $CDCl_3$, epimer of **(*Z*,*E*)-2b**) δ 2.87 (m, 1 H), 2.95 (dq, *J* = 10.3, 8.3 Hz, 1 H), 5.21 (t, *J* = 10.3 Hz, 1 H), 6.09 (dd, *J* = 10.3, 16.6 Hz, 1 H), 6.35 (tm, *J* = 10.3 Hz, 1 H), 9.66 (d, *J* = 2.4 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$, epimer of

(***Z*,*E*)-2b**) δ 24.1, 32.5, 55.7, 128.4, 130.1, 130.8, 131.3, 204.5; HRMS calcd for $C_{11}H_{16}O$-CH_3: 149.0966. Found *m*/*z* (relative intensity) 149.0932 (M^+-CH_3, 83), 135 (100).

2-[(1*E*)-3-Methyl-1,3-butadienyl]cyclopentanecarbaldehyde (**2c**): IR (neat) 2955 (s), 2870 (m), 1720 (s), 1612 (w), 1450 (w), 964 (w), 887 (w) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, **(*E*)-2c**) δ 1.42-2.10 (m, 6 H), 1.83 (s, 3 H), 2.56 (dq, *J* = 2.7, 8.8 Hz, 1 H), 2.80 (dq, *J* = 7.8, 8.8 Hz, 1 H), 4.90 (s, 2 H), 5.60 (dd, *J* = 7.8 Hz, 15.6 Hz, 1 H), 6.17 (d, *J* = 15.6 Hz, 1 H), 9.61 (d, *J* = 2.7 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$, **(*E*)-2c**) δ 18.6, 24.8, 26.2, 33.7, 44.7, 58.0, 115.4, 131.8, 132.9, 141.4, 203.0; ^1H NMR (400 MHz, $CDCl_3$, epimer of **(*E*)-2c**) δ 1.80 (s, 3 H), 2.89 (ddt, *J* = 2.7, 6.1, 8.1 Hz, 1 H), 3.00 (dq, *J* = 6.1, 8.5 Hz, 1 H), 5.64 (dd, *J* = 8.5, 15.6 Hz, 1 H), 6.22 (d, *J* = 15.6 Hz, 1 H), 9.67 (d, *J* = 2.7 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$, epimer of **(*E*)-2c**) δ 24.2, 25.0, 32.5, 46.1, 55.8, 115.6, 129.2, 133.8, 204.3; HRMS calcd for $C_{11}H_{16}O$-CH_3: 149.0966. Found *m*/*z* (relative intensity) 149.0961 (M^+-CH_3, 63), 135 (100).

3-(1,3-Butadienyl)cyclopentanecarbaldehyde (**2e**): (a mixture of *E*- and *Z*- isomers in a ratio of 4 : 1): IR (neat) 2955 (s), 2870 (m), 2176 (w), 1720 (s), 1450 (w), 1003 (s), 903 (m) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, **(*E*)-2e**) δ 1.41 (m, 1 H), 1.60 (m, 1 H), 1.78-1.96 (m, 3 H), 2.04 (dt, *J* = 12.9, 7.1 Hz, 2 H), 2.61 (dquint, *J* = 6.8, 9.8 Hz, 1 H), 2.84 (m, 1 H), 4.98 (d, *J* = 10.3 Hz, 1 H), 5.11 (d, *J* = 17.2 Hz, 1 H), 5.65 (dd, *J* = 7.6, 15.2 Hz, 1 H), 6.07 (dd, *J* = 10.3, 15.2 Hz, 1 H), 6.29 (dt, *J* = 17.2, 10.3 Hz, 1 H), 9.62 (d, *J* = 2.4 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$, **(*E*)-2e**) δ 25.8, 32.5, 33.2, 43.5, 51.3, 115.4, 130.1, 136.8, 137.4, 202.9; ^1H NMR (400 MHz, $CDCl_3$, **(*Z*)-2e**) δ 2.13 (ddd, *J* = 4.6, 7.1, 12.2 Hz, 2 H), 3.02 (m, 1 H), 5.10 (dm, *J* = 10.5 Hz, 1 H), 5.19 (dm, *J* = 16.8 Hz, 1 H), 5.33 (dt *J* = 10.5, 6.3 Hz, 1 H), 5.96 (dt, *J* = 10.5, 4.6 Hz, 1 H), 6.61 (dt, *J* = 16.8, 10.5 Hz, 1 H), 9.64 (d, *J* = 2.0 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$, **(*Z*)-2e**) δ 25.9, 33.2, 33.9, 38.9, 51.5, 117.4, 128.9, 135.6, 202.9; HRMS calcd for $C_{10}H_{14}O$: 150.1045 . Found *m*/*z* (relative intensity) 151 (M^++1, 12), 150.1057 (M^+, 100), 149

(1), 121 (10).

***cis*-1,2,2-Trimethyl-3-[(1*E*,3*E*)-4-phenyl-1,3-butadienyl]cyclopentanecarbaldehyde** (**2i**): (mixture of *E*,*E*- and *Z*,*E*- isomers in a ratio of 7 : 1): IR (KBr disk) 3010 (w), 2950 (m), 2850 (w), 1740 (s), 1460 (w), 1440 (m), 1380 (m), 1360 (m), 1300 (w), 1060 (w), 980 (s), 900 (m), 820 (w), 740 (s), 680 (s) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, **(*E*,*E*)-2i**) δ 0.82 (s, 3 H), 1.00 (s, 3 H), 1.10 (s, 3 H), 1.39 (ddd, *J* = 5.1, 9.2, 13.9 Hz, 1 H), 1.67 (dddd, *J* = 5.1, 9.2, 11.7, 13.9 Hz, 1 H), 1.96 (ddt, *J* = 5.1, 13.9, 9.2 Hz, 1 H), 2.45 (ddd, *J* = 5.1, 11.7, 13.9 Hz, 1 H), 2.56 (q, *J* = 9.2 Hz, 1 H), 5.69 (dd, *J* = 9.2, 15.0 Hz, 1 H), 6.21 (dd, *J* = 10.6, 15.0 Hz, 1 H), 6.48 (d, *J* = 15.0 Hz, 1 H), 6.77 (dd, *J* = 10.6, 15.0 Hz, 1 H), 7.21 (tt, *J* = 1.7, 7.0 Hz, 1 H), 7.30 (dt, *J* = 1.7, 7.0 Hz, 2 H), 7.37 (dd, *J* = 1.7, 7.0 Hz, 2 H), 9.65 (s, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$, **(*E*,*E*)-2i**) δ ; 18.8, 19.4, 22.6, 27.5, 30.5, 47.7, 52.0, 58.3, 126.1, 127.1, 128.4, 128.9, 130.7, 132.0, 134.3, 137.3, 205.9; ^1H NMR (400 MHz, $CDCl_3$, **(*Z*,*E*)-2i**) δ .086 (s, 3 H), 1.00 (s, 3 H), 1.17 (s, 3 H), 3.11 (q, *J* = 9.8 Hz, 1 H), 5.36 (t, *J* = 11.0 Hz, 1 H), 6.28 (t, *J* = 11.0 Hz, 1 H), 6.56 (d, *J* = 15.5 Hz, 1 H), 7.00 (dd, *J* = 11.0, 15.5 Hz, 1 H), 9.66 (s, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$, **(*Z*,*E*)-2i**) δ 18.9, 19.3, 22.8, 28.6, 30.8, 46.6, 60.3, 124.2, 126.2, 127.4, 128.5, 130.6, 132.3, 133; HRMS calcd for $C_{19}H_{24}O$: 268.1897. Found *m/z* (relative intensity) 269 (M^++1, 17), 268.1832 (100); Anal calcd for $C_{19}H_{24}O$: C, 84.94; H, 9.09. Found: C, 84.61, H, 9.05.

***cis*-1,2,2-Tirmethyl-3-[(1*E*,3*Z*)-3-methylpenta-1,3-dienyl]cyclopentanecarbaldehyde (2j):** IR (neat) 2950 (s), 2880 (m), 2700 (w), 1760 (m), 1720 (s), 1450 (m), 1370 (m), 960 (w), 900 (w), 840 (w), 780 (w) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.80 (s, 3 H), 0.96 (s, 3 H), 1.08 (s, 3 H), 1.37 (ddd, *J* = 5.5, 9.2, 13.9 Hz, 1 H), 1.65 (dddd, *J* = 5.5, 9.2, 11.7, 13.9 Hz, 1 H), 1.71 (dd, *J* = 1.5, 7.0 Hz, 1 H), 1.80 (t, *J* = 1.5 Hz, 3 H), 1.92 (ddt, *J* = 5.1, 13.9, 9.2 Hz, 1 H), 2.43 (ddd, *J* = 5.1, 11.7, 13.9 Hz, 1 H), 2.50 (q, *J* = 9.2 Hz, 1 H), 5.34 (q, *J* = 7.0 Hz, 1 H), 5.48 (dd,

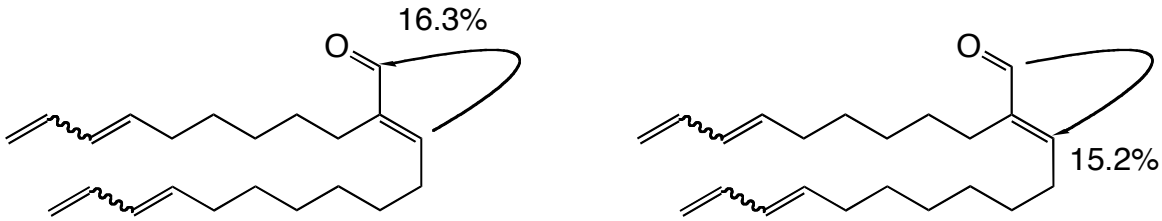
J = 9.2, 15.4 Hz, 1 H), 6.41 (d, *J* = 15.4 Hz, 1 H), 9.66 (s, 1 H). NOE: C3*'Me* (8.3%) by irradiation at C1'H; C4'*Me* (14.6%) and C4'H (0%) by irradiation at C2'H; HRMS calcd for $C_{15}H_{24}O$: 220.1827. Found *m/z* (relative intensity) 220.1827 (M^+, 100), 205 (10), 192 (45), 177 (43), 152 (31), 109 (88), 108 (53).

***cis*-1-Acetyl-3-[*(E)*-1,3-butadienyl]-1,2,2-trimethylcyclopentane (2k):** IR (neat) 2950 (s), 2860 (m), 1700 (s), 1650 (w), 1600 (w), 1460 (m), 1350 (m), 1230 (m), 1080 (m), 1000 (s) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.67 (s, 3 H), 1.06 (s, 3 H), 1.17 (d, *J* = 0.7 Hz, 3 H), 1.39 (ddd, *J* = 5.1, 9.2, 13.6 Hz, 1 H), 1.57 (dddd *J* = 5.1, 9.2, 11.7, 13.6 Hz, 1 H), 1.83 (ddt, *J* = 5.5, 13.6, 9.2 Hz, 1 H), 2.10 (s, 3 H), 2.48 (q, *J* = 9.2 Hz, 1 H), 2.55 (ddd, *J* = 5.5, 11.7, 13.7 Hz, 1 H), 5.00 (dd, *J* = 1.8, 10.3 Hz, 1 H), 5.10 (dd, *J* = 1.8, 17.2 Hz, 1 H), 5.59 (dd, *J* = 9.2, 15.4 Hz, 1 H), 6.03 (ddd, *J* = 1.8, 10.3, 15.4 Hz, 1 H), 6.33 (dt, *J* = 17.2, 10.3 Hz, 1 H); HRMS calcd for $C_{14}H_{22}O$: 206.1671. Found *m/z* (relative intensity) 206.1676 (M^+, 100), 191 (14), 122 (18), 83 (70); Anal. Calcd for $C_{14}H_{22}O$: C, 81.50; H, 10.75. Found: C, 81.51; H, 10.83.

2-(5,7-Octadienyl)-(2*E*,9,11)-decatienal (3s): (a mixture of *E*- and *Z*- isomers in a ratio of 7 : 1): IR (neat) 3086 (w), 3009 (m), 2932 (s), 2855 (s), 1690 (s), 1643 (m), 1458 (w), 1003 (s), 895 (m) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, **(*E*)-3s**) δ 1.30-1.46 (m, 4 H), 1.50 (quint, *J* = 7.3 Hz, 2 H), 2.09 (quint, *J* = 6.6 Hz, 4 H), 2.23 (t, *J* = 7.3 Hz, 2 H), 2.34 (q, *J* = 7.3 Hz, 2 H), 4.94 (d, *J* = 10.3 Hz, 1 H), 4.96 (d, *J* = 10.3 Hz, 1 H), 5.07 (d, *J* = 16.8 Hz, 1 H), 5.08 (d, *J* = 16.8 Hz, 1 H), 5.67 (dt, *J* = 15.1, 7.3 Hz, 1 H), 5.69 (dt, *J* = 15.1, 7.3 Hz, 1 H), 6.03 (dd, *J* = 5.6, 15.1 Hz, 1 H), 6.05 (dd, *J* = 5.6, 15.1 Hz, 1 H), 6.28 (ddd, *J* = 5.6, 10.3 Hz, 16.8 Hz, 1 H), 6.31 (ddd, *J* = 5.6, 10.3, 16.8 Hz, 1 H), 6.42 (t, *J* = 7.3 Hz, 1 H), 9.35 (s, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$, **(*E*)-3s**) δ 28.2, 28.5, 28.9, 29.1, 32.2, 32.3, 114.6, 114.7, 131.0, 131.1, 134.8, 137.0, 137.1, 143.5, 154.9, 194.9; ^1H NMR (400 MHz, $CDCl_3$, **(*Z*)-3s**) δ 2.37 (q, *J* = 7.6 Hz, 2

H), 5.16 (d, *J* = 17.1 Hz, 1 H), 5.18 (d, *J* = 17.1 Hz, 1 H), 5.43 (dt, *J* = 9.6, 7.6 Hz, 2 H), 6.62 (dt, *J* = 16.8, 10.3 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$, **(*Z*)-3s**) δ 27.5, 28.2, 29.5, 29.6, 116.7, 116.8, 129.2, 129.3, 132.0, 132.1, 132.3.

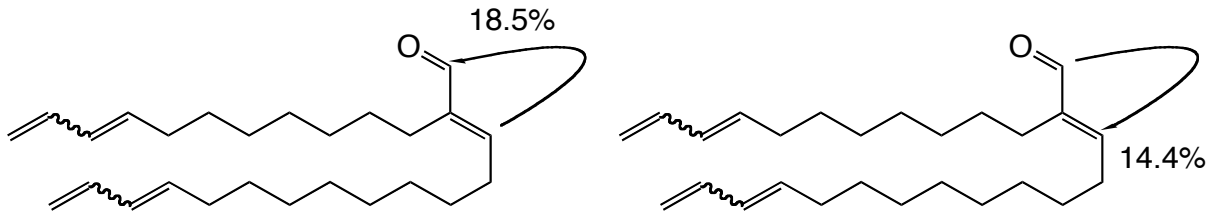
2-(6,8-Nonadecadienyl)-(2*E*,10,12)-tridecatrienal (**3t**): (a mixture of *E*- and *Z*- isomers in a ratio of 3 : 1): IR (neat) 3307 (w), 2928 (s), 2855 (s), 1688 (s), 1308 (s), 1003 (s), 897 (m), 701 (w); cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, **(*E*)-3t**) δ 1.22-1.68 (m, 14 H), 2.07 (br dt, *J* = 14.3, 7.1 Hz, 4 H), 2.22 (t, *J* = 7.3 Hz, 2 H), 2.34 (q, *J* = 7.3 Hz, 2 H), 4.95 (d, *J* = 10.3 Hz, 2 H), 5.08 (d, *J* = 16.8 Hz, 2 H), 5.68 (ddt, *J* = 3.7, 15.1, 7.1 Hz, 2 H), 6.04 (ddd, *J* = 4.9, 10.3, 15.1 Hz, 2 H), 6.30 (ddt, *J* = 1.5, 16.8, 10.3 Hz, 2 H), 6.42 (t, *J* = 7.3 Hz, 1 H), 9.75 (t, *J* = 1.7 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$, **(*E*)-3t**) δ 28.6, 28.6, 28.8, 28.9 , 29.0, 29.2, 32.4, 114.5, 114.6, 130.9, 135.0, 135.1, 137.1, 143.6, 154.9, 195.0; ^{1}H NMR (400 MHz, $CDCl_3$, **(*Z*)-3t**) δ 5.17 (dm, *J* = 16.8 Hz, 2 H), 5.44 (dd, *J* = 7.3, 11.0 Hz, 2 H), 6.62 (dt, *J* = 16.8 Hz, 10.0 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$, **(*Z*)-3t**) δ 29.3, 29.4, 30.9, 32.7, 117.5, 127.3, 130.3, 132.1, 132.6, 133.7, 137.8, 148.5; HRMS calcd for $C_{22}H_{34}O_2$: 314.2610. Found *m/z* (relative intensity) 315 (M^++1, 28), 314.2594 (M^+, 100), 313 (3), 285 (8).



NOE Increments (%) Observed for **3t**

2-(8,10-Undecadienyl)-(2*E*,12,14)-pentadecatrienal (**3u**): (a mixture of *E*- and *Z*- isomers in a ratio of 3 : 1): IR (neat) 2926 (s), 2855 (s), 1726 (s), 1688 (s), 1641 (m), 1441 (s), 1308 (s), 1003 (s), 899 (s), 700 (s) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, **(*E*)-3u**) δ 1.22- 1.68 (m, 22 H), 2.03 (m, 4 H), 2.22 (t, *J* = 7.3 Hz, 2 H), 2.34 (q, *J* = 7.3 Hz, 2 H), 4.94 (d, *J* = 10.3 Hz, 2 H),

5.08 (d, *J* = 17.1 Hz, 2 H), 5.69 (dt, *J* = 15.1, 7.3 Hz, 2 H), 6.03 (ddm, *J* = 10.3, 15.1 Hz, 2 H), 6.42 (t, J = 7.3 Hz, 1 H), 6.30 (dt, *J* = 17.1, 10.3 Hz, 2 H), 9.75 (t, *J* = 2.0 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$, **(*E*)-3u**) δ 27.7, 28.7, 28.9, 29.1, 29.3, 29.6, 32.5, 114.4, 114.5, 130.7, 130.8, 135.3, 137.2, 143.7, 155.0, 195.0; ^{1}H NMR (400 MHz, $CDCl_3$, **(*Z*)-3u**) δ 5.17 (d, *J* = 16.7 Hz, 2 H), 5.54 (dt, J = 11.0, 7.3 Hz, 2 H), 5.99 (br t, *J* = 11.0 Hz, 2 H), 6.62 (dt, *J* = 16.7, 11.0 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$, **(*Z*)-3u**) δ 116.5, 116.6, 129.0, 129.1, 132.2, 132.8 ; HRMS calcd for $C_{26}H_{42}O_2$: 370.3236. Found *m/z* (relative intensity) 371 (M^++1, 29), 370.3238 (M^+, 100), 369 (2), 353 (11).



NOE Increments (%) Observed for **3u**

2-(10,12-Tridecadienyl)-(2*E*,14,16)-heptadecatrienal (**3v**): (a mixture of *E*- and *Z*- isomers in a ratio of 2 : 1): IR (neat) 2926 (s), 2855 (s), 1728 (m), 1688 (m), 1308 (m), 1003 (m), 897 (m), 700 (w) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, **(*E*)-3v**) δ 1.20-1.44 (m, 28 H), 1.62 (quint, *J* = 7.3 Hz, 2 H), 2.07 (q, *J* = 7.3 Hz, 2 H), 2.17 (q, *J* = 7.3 Hz, 2 H), 2.22 (t, *J* = 7.3 Hz, 2 H), 2.34 (q, *J* = 7.3 Hz, 2 H), 4.94 (d, *J* = 10.3 Hz, 2 H), 5.07 (d, *J* = 16.8 Hz, 2 H), 5.69 (dt, *J* = 15.1, 7.3 Hz, 2 H), 6.04 (ddd, *J* = 0.7, 10.3, 15.1 Hz, 2 H), 6.30 (dt, *J* = 16.8, 10.3 Hz, 2 H), 6.42 (t, *J* = 7.3 Hz, 1 H), 9.35 (s, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$, **(*E*)-3v**) δ 28.7, 28.9, 29.2, 29.4, 29.5, 29.6, 32.5, 114.4, 130.7, 135.4, 137.2, 143.7, 155.0, 195.0; ^{1}H NMR (400 MHz, $CDCl_3$, **(*Z*)-3v**) δ 5.07 (d, *J* = 10.6 Hz, 2 H), 5.16 (d, *J* = 16.8 Hz, 2 H), 5.44 (dt, *J* = 10.6, 7.3 Hz, 2 H), 5.99 (t, *J* = 10.6 Hz, 2 H), 6.63 (dt, *J* = 16.8, 10.3 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$, **(*Z*)-3v**) δ 116.5, 129.0, 132.2, 132.8, 132.9.

2-Ethyl-decahydro-4-vinyl-4*H*-cyclodeca[*d*][1,3,2]dioxaborinine (**4**): IR (neat) 3100 (w),

2930 (s), 1405 (s), 1338 (s), 1290 (s), 1220 (s), 990 (m), 930 (m), 764 (w) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, major isomer) δ 0.70 (q, *J* = 7.6 Hz, 2 H), 0.92 (t, *J* = 7.6 Hz, 3 H), 1.30-1.80 (m, 15 H), 1.81 (dt, *J* = 13.4, 4.6 Hz, 1 H), 1.89 (ddd, *J* = 3.7, 7.1, 10.7 Hz, 1 H), 4.08 (ddd, *J* = 3.7, 4.6, 9.3 Hz, 1 H), 4.29 (m, 1 H), 5.23 (d, *J* = 10.5 Hz, 1 H), 5.25 (dt, *J* = 17.1, 1.5 Hz, 1 H), 5.86 (ddd, *J* = 4.6, 10.5, 17.1 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$, a mixture of 4 isomers) δ 7.9, 20.7, 21.3, 22.0, 22.4, 22.6, 23.3, 23.8, 24.3, 24.4, 24.6, 24.7, 24.8, 24.9, 25.0, 25.3, 25.4, 25.9, 26.0, 26.1, 27.5, 30.0, 30.9, 31.1, 38.7, 39.8, 41.3, 43.5, 70.0, 72.3, 74.0, 74.7, 75.1, 75.8, 76.3, 77.1, 78.2, 114.5, 115.3, 116.7, 135.6, 137.3, 138.1, 139.0; HRMS calcd for $C_{15}H_{27}BO_2$: 250.2104. Found *m/z* (relative intensity) 251 (M^++1, 11), 250.2087 (M^+, 51), 249 (13), 235 (8), 221 (100).

Decahydro-2-phenyl-4-vinyl-4*H*-cyclodeca[*d*][1,3,2]dioxaborinine (**5**): IR (neat) 3076 (w), 2930 (m), 1601 (w), 1441 (m), 1306 (m), 1130 (w), 1028 (w), 989 (w), 924 (w), 700 (m), 646 (m) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, major isomer) δ 1.32- 1.90 (m, 15 H), 1.95 (m, 1 H), 2.00 (ddd, *J* = 4.2, 6.8, 11.2 Hz, 1 H), 4.27 (ddd, *J* = 3.2, 4.9, 9.3 Hz, 1 H), 4.49 (m, 1 H), 5.26 (dt, *J* = 10.5, 1.5 Hz, 1 H), 5.32 (dt, *J* = 17.1, 1.5 Hz, 1 H), 5.95 (ddd, *J* = 4.6, 10.5, 17.1 Hz, 1 H), 7.33 (tm, *J* = 7.6 Hz, 2 H), 7.41 (tm, *J* = 7.6 Hz, 1 H), 7.82 (dm, *J* = 7.6 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$, a mixture of 4 isomers) δ 17.8, 20.8, 21.5, 22.1, 22.5, 22.7, 23.3, 23.8, 24.0, 24.3, 24.4, 24.6, 24.7, 24.8, 24.9, 25.0, 25.2, 25.4, 25.6, 25.8, 25.9, 26.0, 26.1, 26.2, 26.4, 26.6, 26.7, 27.1, 27.5, 28.1, 28.3, 29.9, 30.0, 30.1, 30.5, 30.9, 31.1, 38.1, 39.0, 40.1, 41.4, 42.1, 42.5, 43.6, 44.1, 69.7, 70.5, 70.7, 72.7, 72.9, 73.8, 74.2, 74.4, 75.1, 75.5, 76.1, 76.8, 77.1, 78.5, 114.6, 114.7, 115.0, 115.4, 115.5, 116.7, 116.9, 117.7, 127.3, 127.4, 130.3, 130.4, 133.7, 135.4, 136.3, 137.2, 137.4, 137.5, 138.0, 138.6, 138.8; HRMS calcd for $C_{19}H_{27}BO_2$: 298.2104. Found *m/z* (relative intensity) 299 (M^++1, 20), 298.2088 (M^+, 100), 297 (26), 283 (4).

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[8] Crystallographic data of **1k** has been deposited with the Cambridge Crystallographic Data

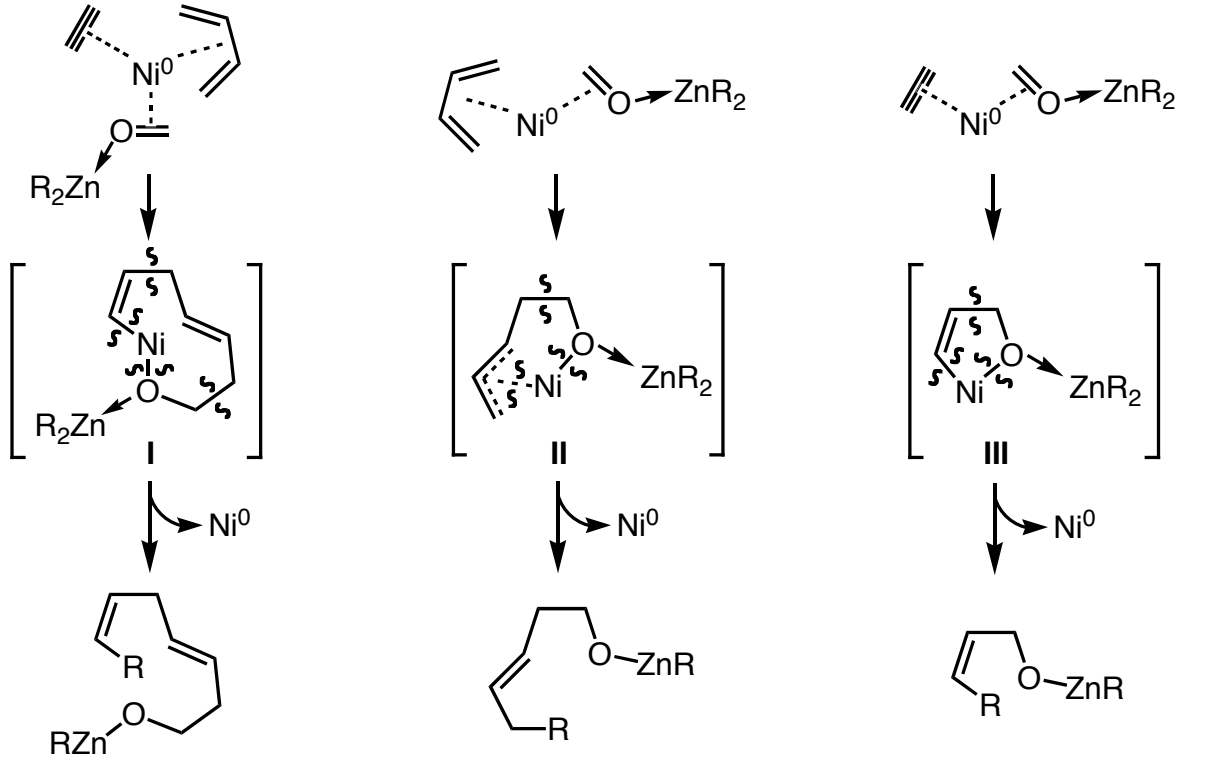
Center as supplementary publication number CCDC-631058. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, U.K. (fax: (+41)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

第３章

ニッケル触媒を用いるジメチル亜鉛、１，ω－ジエンイン、カルボニル化合物の四成分連結反応

３－１　緒言

後周期遷移金属であるニッケル触媒は、アルキンやジエンのオリゴメリ化や環化異性化に有効であり、効率の良い反応が数多く報告されているが、[1],[2]　カルボニル化合物に対する求核付加反応において触媒作用を示す例は極めて稀である。チタンやジルコニウムのような前周期遷移金属は、カルボニル化合物の反応に頻繁に用いられ、オキサメタラサイクルを中間体とする炭素－炭素結合形成反応が数多く報告されている。[1],[3],[4]　これは、前周期遷移金属の高い酸素親和性が寄与するところが大きい。しかし、それらの多くは量論的な反応である。Montgomery 教授らは、ニッケル触媒、有機亜鉛を用いるアルキンとカルボニル化合物の還元的カップリング反応を開発し、位置および立体選択的に多置換アリルアルコールを合成できることを報告した（Scheme 1, c）。[5],[6]　これに対して、当研究室では、ニッケル触媒、ジメチル亜鉛共存下、１，３－ジエン、カルボニル化合物を反応させると、三成分連結反応が位置及び立体選択的に進行し、ホモアリルアルコール誘導体を与えることを報告した（Scheme 1, b）。[7]　さらに当研究室では、ニッケル触媒存在下、これらの反応で用いる全ての基質を反応させると、ジメチル亜鉛、アルキン、１，３－ジエン、カルボニル化合物の四成分連結反応が位置及び立体選択的に進行することを発見した（Scheme 1, a）。[8]　いろいろな組み合わせの生成物ができる可能性があるが、エントロピー的に最も不利な四成分連結反応が優先的に進行することは非常に興味深い。

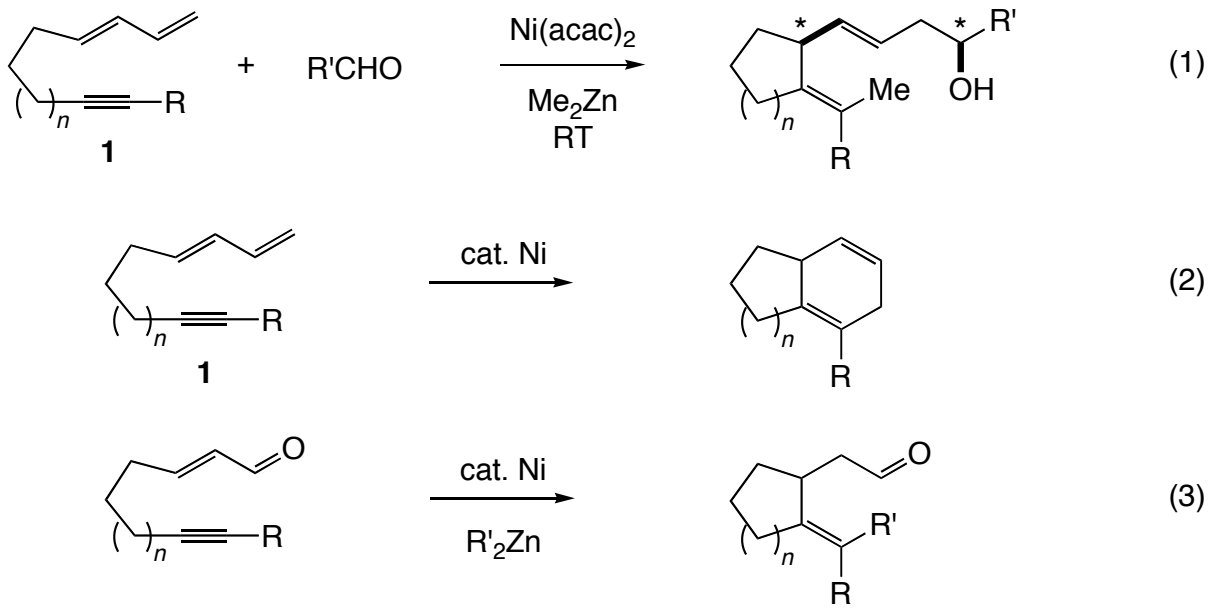


(a) Present Work　　(b) Our Previous Work　　(c) Montgomery's Work

Scheme 1. Nickel-Catalyzed Multi-Component Connection Reactions

著者は、ニッケル触媒、ジメチル亜鉛共存下、１，３－ジエン、アルキン骨格を併せ持つ基質である１，ω－ジエンインとカルボニル化合物を反応させると、分子内四成分連結反応が位置および立体選択的に進行し、高収率で環化生成物を与えることを発見した（Scheme 2、式１）。[12]　メチル基はジエン由来の置換基に対してアルキンにシス付加する。この反応で最も興味深い点は、ニッケル触媒により、一挙にジメチル亜鉛、アルキン、１，３－ジエン、カルボニル化合物が反応し、新たに３種類のC－C 結合が形成するだけでなく、＊印で示す炭素間で極めて高い遠隔位１，５－*syn* ジアステオ選択性が発現することである。一般に、この種の反応では、五員環形成は容易であるが、六員環形成は困難である場合が多い。ところが、本反応は、多彩な置換様式、原子組成を持つ六員環化合物の合成にも広く応用できる。類似の反応例として、玉尾教授らによる [４＋２]環化付加反応（Scheme 2、式２）、[9]　Montgomery

教授らのω-yne-enone の求核的環化反応がある（Scheme 2、式３）。[10]　これらの反応が二成分、三成分連結反応であるのに対して、本反応は、ジメチル亜鉛、アルキン、１，３－ジエン、カルボニル化合物の四成分が一挙に連結するという対比を示し、ニッケル触媒の多彩な反応性を示す興味深い知見である。



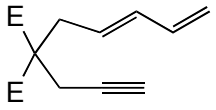
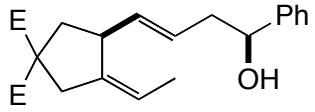
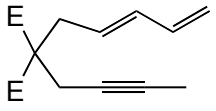
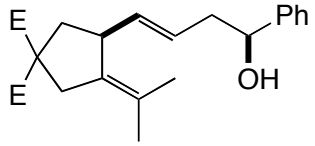
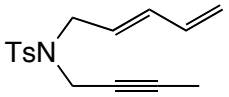
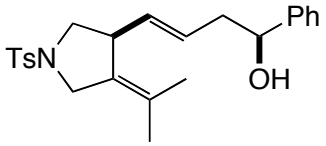
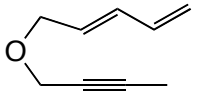
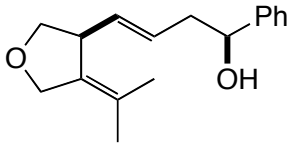
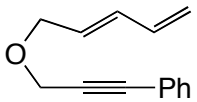
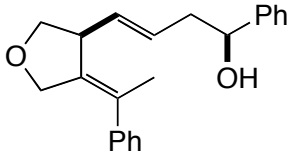
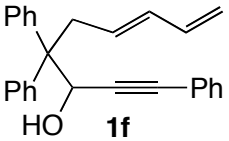
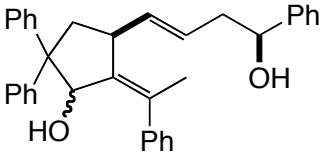
Scheme 2. Nickel-Catalyzed Cyclization of 1,ω-Dienynes **2** and 1,ω-Alkyn-enals

本章では、種々の１，ω－ジエンイン、カルボニル化合物を用いた分子内四成分連結反応の反応性、選択性について報告する。

２．結果及び考察

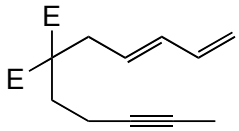
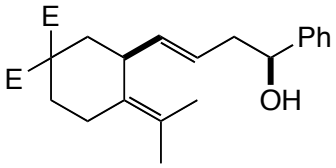
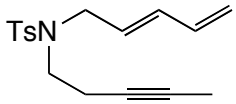
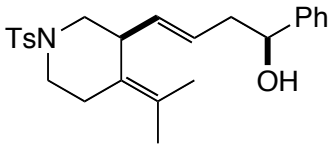
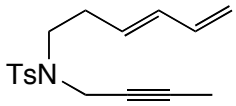
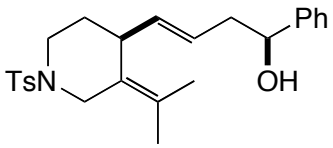
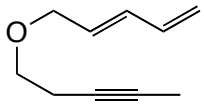
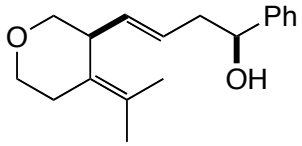
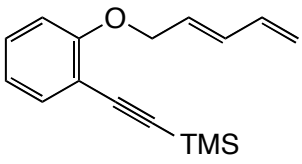
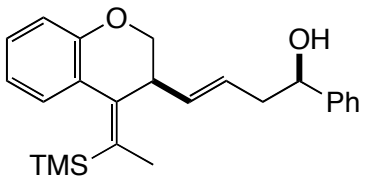
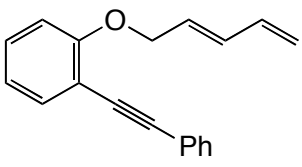
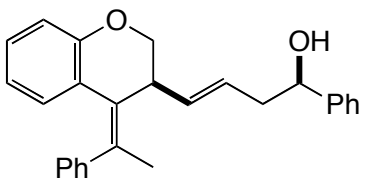
触媒量の Ni(acac)$_2$ (0.1 mmol)、ジメチル亜鉛 (2.4 mmol)、ベンズアルデヒド (2 mmol)を用いて、１，ω－ジエンイン **1** (1 mmol)の検討を行った（Table 1, Table 2）。

Table 1. Nickel-Catalyzed Conjugative Addition of Me_2Zn toward Benzaldehyde across 1,ω-Dienynes **1**: Formation of Five-Membered Ring[a]

Run	1,ω-Dienyne **1**	Time (h)	Product **2**[b] (% Isolated) [ratio][c]
1	 **1a**	1	 **2a**: 45 [11 : 1]
2	 **1b**	1	 **2b**: 63 [8 : 1]
3	 **1c**	1	 **2c**: 67 [>30 : 1]
4	 **1d**	0.5	 **2d**: 70 [>30 : 1]
5	 **1e**	1	 **2e**: 61 [>30 : 1]
6	 **1f**	3.5[d]	 **2f**: 77 [4 : 1][e]

[a] Reaction conditions: **1** (1 mmol), benzaldehyde (2 mmol), Ni(acac)$_2$ (10 mol%), Me_2Zn (2.4 mmol, 1 M hexane) in THF (5 ml) at room temperature under N_2. E stands for CO_2Et. [b] Yield refers to the isolated, spectroscopically homogeneous material. [c] Diastereomeric ratio determined by ^{1}H NMR (400 MHz). Only the major isomers are shown. [d] Me_2Zn (3.6 mmol) was applied. [e] Diastereomers arising from the configrational isomerism of the carbon bearing the OH group.

Table 2. Nickel-Catalyzed Conjugative Addition of Me_2Zn toward Benzaldehyde across 1,ω-Dienynes **1**: Formation of Six-Membered Ring[a]

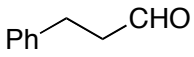
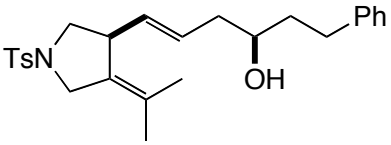
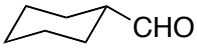
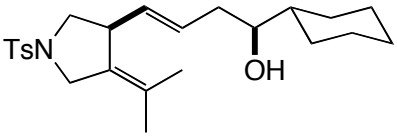
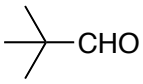
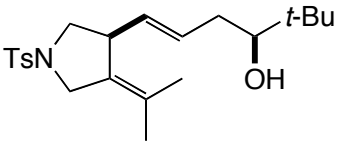
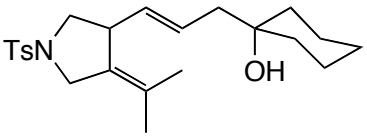
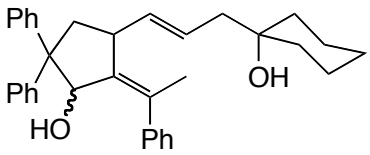
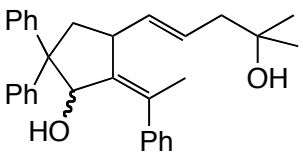
Run	1,ω-Dienyne **1**	Time (h)	Product **2**[b] (% Isolated) [ratio][c]
1	 **1g**	1	 **2g**: 83 [8 : 1]
2	 **1h**	1	 **2h**: 96 [single]
3	 **1i**	1	 **2i**: 60 [7 : 1]
4	 **1j**	1	 **2j**: 60 [single]
5	 **1k**	19	 **2k**: 65 [10 : 1]
6	 **1*l***	2	 **2*l***: 61 [10 : 1]

[a] For reaction condition, see footnote a in Table 1. E, Ts, and TMS stand for CO_2Et, *p*-toluenesulfonyl, and trimethylsilyl groups, respectively. [b] Yield refers to the isolated, spectroscopically homogeneous material. [c] Diastereomeric ratio determined by ^1H NMR (400 MHz). Only the major isomers are shown.

末端アルキン **1a** を用いた場合、低収率ながら、環化生成物 **2a** を与えた（Table 1, Run 1）。反応は位置及び立体選択的に進行し、ジエンの末端炭素がベンズアルデヒドに付加し、ジメチル亜鉛のメチル基はジエン由来の置換基に対してアルキンに対してシス付加する。さらに、側鎖のオレフィンは *E* 体である。最も注目すべきことは、高い遠隔位１，５－*syn* ジアステレオ選択性が発現することである。内部アルキン **1b**－**1*l*** を用いた場合には、高収率で五員環及び六員環生成物 **2b**－**2*l*** を与えた（Table 1 Runs 2-6, Table 2 Runs 1-6）。**1d**、**1e**、**1j**－**1*l*** は、分子内にアリルエーテル骨格を有しているため、Ni(0)によるアリル C－O 結合の切断が起こり、様々な反応が進行することが予想されるが、[11]　分子内四成分連結反応のみが進行し、テトラヒドロフラン誘導体 **2d** や **2e**（Table 1, Runs 4 and 5）、テトラヒドロピラン誘導体 **2j**（Table 2, Run 4）、そして、クロマン誘導体 **2k**、**2*l*** を与えた（Table 2, Runs 5 and 6）。反応時間から判断して、**1k** は他の基質と比べ反応性が低下する。これは、**2k** のフェニル基とトリメチルシリル基が接近するために生じる大きな allylic strain[12]が反応の進行を阻害していると考えられる。**1c**、**1h**、**1i** からは、ピロリジン誘導体 **2c** 及びピペリジン誘導体 **2h**、**2i** を与えた（Table 1, Run 3, Table 2, Runs 2 and 3）。本反応は水酸基許容であり、**1f** を用いた反応では、ジメチル亜鉛をさらに１当量過剰に用いることにより、良好な収率で **2f** を与えた（Table 1, Run 6）。

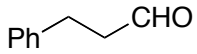
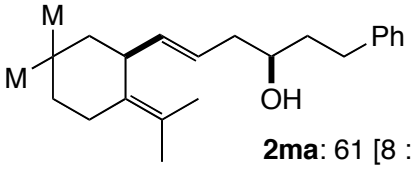
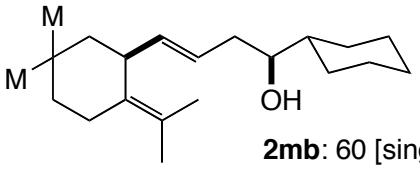
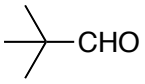
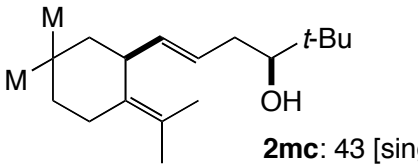
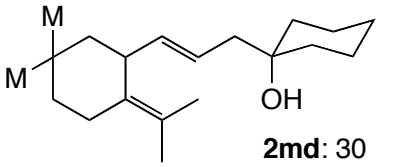
Table 1 と同様の条件下、カルボニル化合物の検討を行った（Table 3, Table 4）。

Table 3. Nickel-Catalyzed Conjugative Addition of Me_2Zn toward Aliphatic Aldehydes and Ketones across **1c** and **1f** Forming Five-Membered Ring Compounds[a]

Run	Carbonyl	Time (h)	Product **2**[b] (% Isolated) [ratio][c]
1		1	 **2ca**: 70 [>30 : 1]
2		1	 **2cb**: 75 [>30 : 1]
3		1	 **2cc**: 70 [>30 : 1]
4		1	 **2cd**: 40
5		22	 **2fd**: 54 [6 : 1][d]
6		22	 **2fe**: 50 [3 : 1][d]

[a] Reaction conditions: **1c** or **1f** (1 mmol), an aliphatic aldehyde or an aliphatic ketone (2 mmol), $Ni(acac)_2$ (10 mol%), Me_2Zn (2.4 mmol for **1c** and 3.6 mmol for **1f**, 1 M hexane) in THF (5 ml) at room temperature under N_2. [b] Yield refers to the isolated, spectroscopically homogeneous material. [c] Diastereomeric ratio determined by ^1H NMR (400 MHz). Only the major isomers are shown. [d] Diastereomer due to OH stereochemistry.

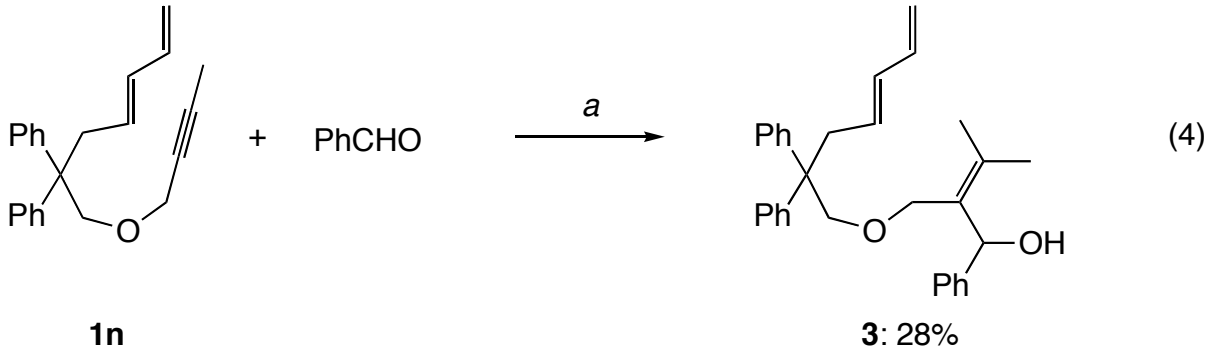
Table 4. Nickel-Catalyzed Conjugative Addition of Me_2Zn toward Aliphatic Aldehydes and Ketones across 2-[(2*E*,4)-Pentadienyl]-2-(3-pentynyl)malonic Acid Dimethyl Ester (**1m**) Forming Six-Membered Ring Compounds[a]

Run	Carbonyl	Time (h)	Product **2**[b] (% Isolated) [ratio][c]
1		1	 **2ma**: 61 [8 : 1][d]
2		1	 **2mb**: 60 [single]
3		4	 **2mc**: 43 [single]
4		5	 **2md**: 30

[a] Reaction conditions: **1m** (1 mmol), an aliphatic aldehyde or an aliphatic ketone (2 mmol), $Ni(acac)_2$ (10 mol%), Me_2Zn (2.4 mmol, 1 M hexane) in THF (5 ml) at room temperature under N_2. [b] Yield refers to the isolated, spectroscopically homogeneous material. [c] Diastereomeric ratio determined by ^1H NMR (400 MHz). Only the major isomers are shown. [d] M stands for CO_2Me.

脂肪族アルデヒドを用いても、芳香族アルデヒドの場合と同様に反応し、良好な収率で五員環生成物並びに六員環生成物を与えた（Table 3, Runs 1-3, Table 4, Runs 1-3）。また、本反応は反応性が低いケトンに対しても適用が可能であり、低収率ながら、目的生成物を与えた（Table 3, Runs 4-6, Table 4, Run 4）。

さらに、１，ω－ジエンイン **1n**、**1o**、**1p** を用いて七員環及び八員環形成を試みた（Scheme 3）。



1n　　**3**: 28%

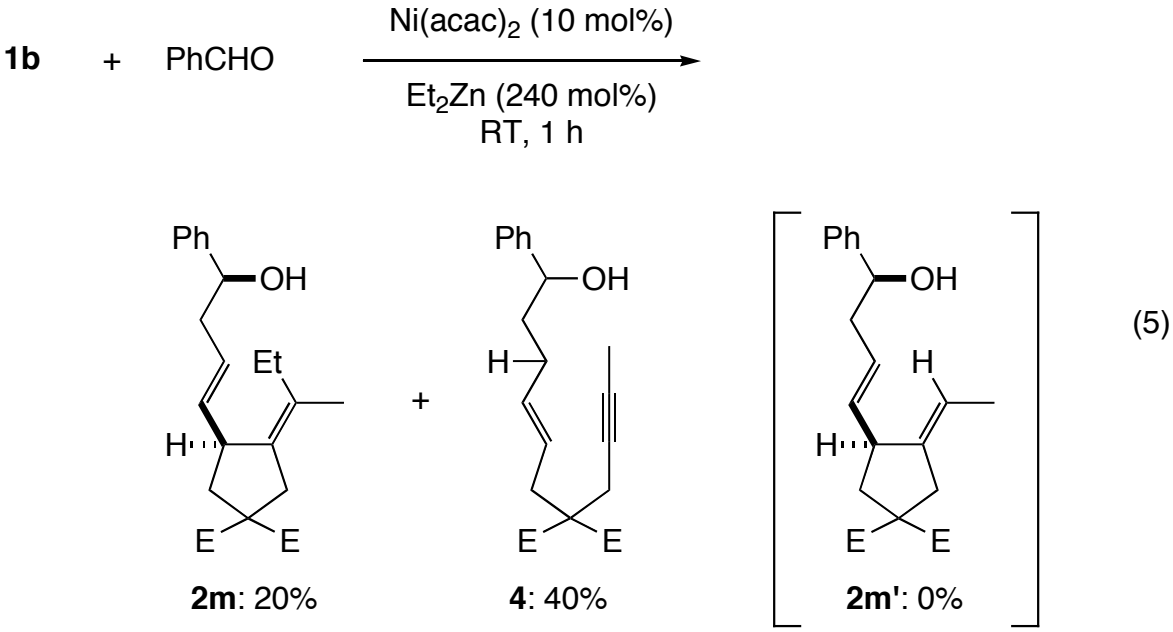
[a] $Ni(acac)_2$ (10 mol%), Me_2Zn (2.4 mmol), RT, 2 h

1o　　**1p**

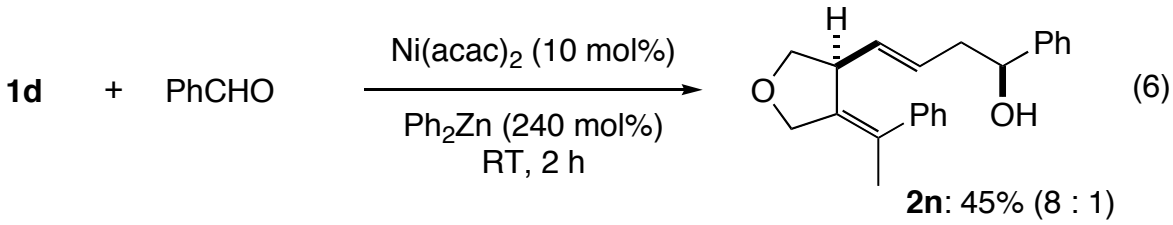
Scheme 3. Attempts for Seven- and Eight-Membered Ring Formation

Ingold-Thrope 効果（*gem*－ジアルキル効果）[13]を利用して環化を促進するために **1n** を用いて反応を行った。**1n** は室温で速やかに反応したが、七員環生成物を与えず、ジメチル亜鉛、アルキン、そして、ベンズアルデヒドの三成分が反応した **3** を低収率で与えた（式４）。また、アルキンとジエンが互いに近接するように、シクロヘキサン及びシクロペンタンにビシナル置換した **1o**、**1p** を用いて反応を行った。溶媒を高希釈条件であるにも拘らず、反応は非常に複雑となり、八員環生成物の単離には至らなかった。

次に、ジエチル亜鉛、ジフェニル亜鉛を用いて検討を行った。常圧窒素雰囲気下、ニッケルアセチルアセトナト（0.1 mmol）、１，ω－ジエンイン **5d** または **5d**（1 mmol）、ベンズアルデヒド（2 mmol）、ジエチル亜鉛またはジフェニル亜鉛（2.4 mmol）、溶媒にテトラヒドロフラン（5 ml）を用いて反応を行った（式５、６）。



(5)



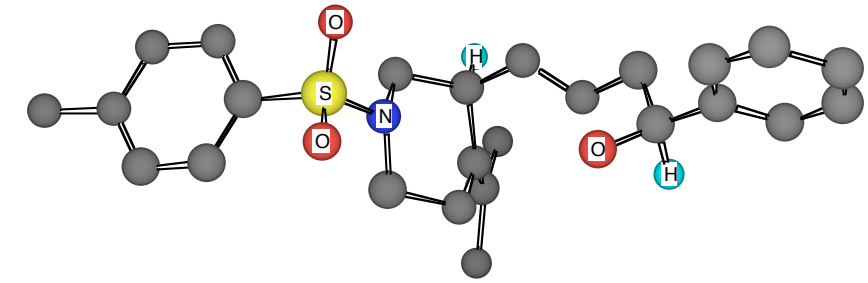
(6)

β－水素を持つジエチル亜鉛を用いた場合、四成分連結反応によるエチル基が導入した **2m** が２０％、ジエチル亜鉛、１，３－ジエン、アルデヒドのホモアリル化反応[6b,c,d]によるビスホモアリルアルコール **4** が４０％得られた（式５）。興味深いことに、アルキンに水素が付加した環化生成物 **2m'**は得られなかった。この結果は、ホスフィン配位子が存在しない場合、アルキルビニルニッケル中間体は、β－水素脱離ではなく還元的脱離が進行するという Montgomery 教授らの報告に一致する。[10]　ジフェニル亜鉛を用いた場合、四成分連結反応が速やかに進行し、フェニル基が導入した

環化生成物 **2n** が得られた。**2e**（Table 1, Run 5）と **2n**（式６）は環外四置換アルケンに関する立体異性体であり、基質および有機亜鉛を使い分けることにより、四置換アルケンを立体選択的に合成できる点からも、本反応の有用性は極めて高い。

２．生成物の構造決定

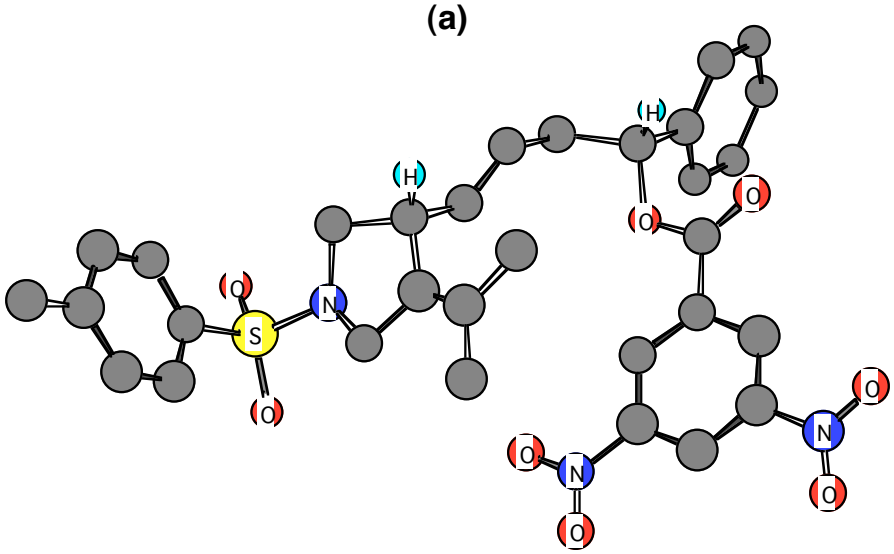
ピペリジン誘導体 **2h** は結晶性が良く、その立体構造は単結晶 X－線構造解析により決定した（Figure 1, a）。[14] また、**2c**、**2i** は３，５－ジニトロ安息香酸エステルに誘導し、X－線構造解析により立体構造を決定した（Figure 1, b）。その結果、環の大きさによらず､環状のアリル位メチン炭素に結合した側鎖とその側鎖の水酸基の１，５位の相対立体配置が、*syn* 体であることが明らかになった。



2h

CCDC 178844

(a)



2c

CCDC 201806

(b)

Figure 1. The Chem 3D™ Presentation of X-Ray Structure of **2h** (a) and a 3,5-Dinitrobenzoic Acid Ester of **2c** (b). For clarity, all protons except those on the stereogenic centers are omitted.

2a の環外二重結合の立体化学は NOE の測定により決定した（Figure 2）。

Ha、Hb への照射で、ビニルプロトンにそれぞれ 8.9%、8.0%の NOE が観測された。一方、メチル基プロトンに対して NOE は観測されなかった。**2e** の立体化学も同様に NOE の測定により決定した。Ha、Hb への照射で、ベンゼン環のオルト位プロトンにそれぞれ 5.3%、3.1%の NOE が観測された。この結果より、ジメチル亜鉛のメチル基は、アルキンとジエン部位の間に新しく形成される単結合に対してシス付加することが明らかになった。

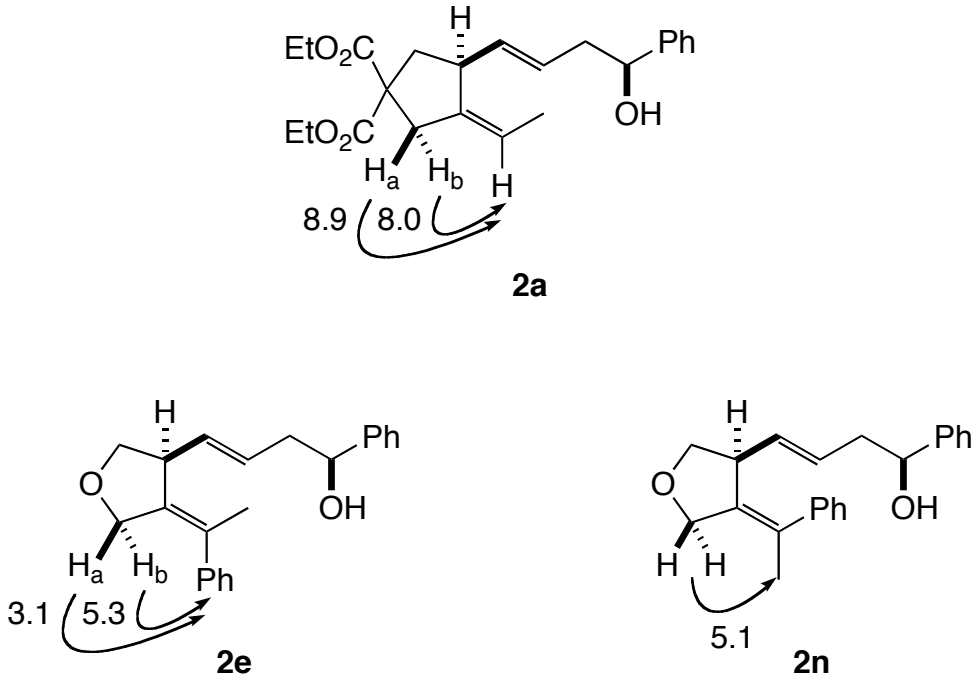
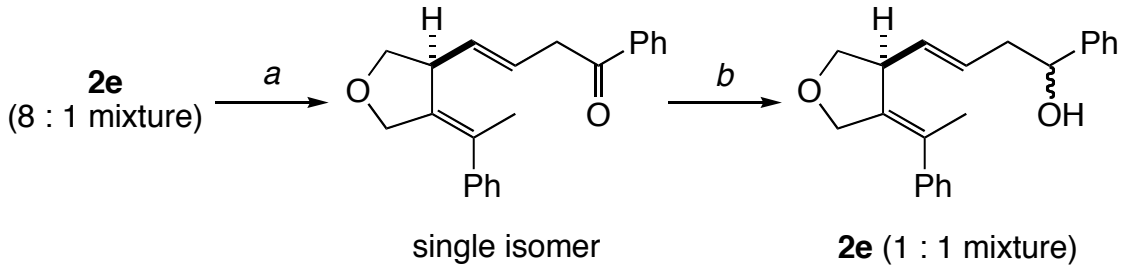


Figure 2. NOE Increments (%) Observed for Products.

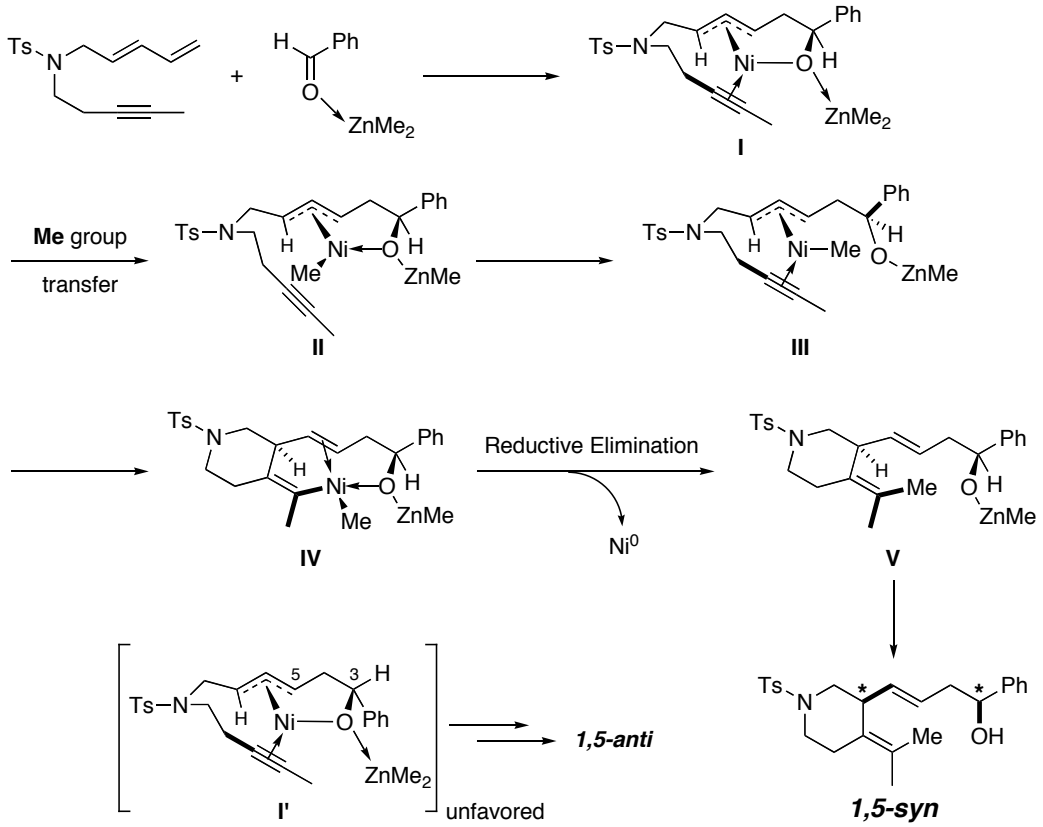
2e の 8：1 の立体異性体の混合物を PCC 酸化によりケトンに誘導して、単一物であることを確認し、続いて、$NaBH_4$ で還元して、**2e** の立体異性体の生成比を ^{1}H NMR および ^{13}C NMR で確認したところ、異性体比が１：１の混合物であったことから、本反応で得られる二種類の立体異性体は、シクロアルカンのメチン炭素と側鎖の水酸基が結合した炭素に関するジアステレオマーであり、二重結合の幾何異性によるものではないことが明らかになった（Scheme 4）。



[a] PCC, CH_2Cl_2, 0 ºC, 2 h (48%); [b] $NaBH_4$, MeOH, RT, 2 h (80%)

Scheme 4. Confirmation of the Structure of the Minor Isomer of **2e**.

四成分連結反応における位置選択性及び立体選択性から判断して、次の反応機構を推定した（Scheme 6）。Ni(0)が１，ω－ジエンインに配位してジエン部位が求核活性化し、ジメチル亜鉛がルイス酸として作用し、カルボニル基に配位してアルデヒドを親電子活性化する。ジエンとアルデヒドに対して、Ni(0)の酸化的環化が進行し、オキサニッケラサイクル中間体 **I** 形成する。１，５位の立体規制は中間体 **I** の構造に由来している可能性が高い。1,5-*anti* 体に導く中間体 **I'**は、アルデヒドの置換基と C５位炭素がゴーシュの関係で不安定あると考えられる。次に、ジメチル亜鉛のメチル基がニッケルに転位して、アルキンがニッケルに配位した中間体 **III** を形成する。**III** のπ－アリルニッケル部位がアルキンに対してシス付加して、メチルビニルニッケル中間体 **IV** を形成し、還元的脱離を受けて、生成物と Ni(0)を与える。再生した Ni(0)は新しい触媒サイクルに利用される。このようにして、反応が立体選択的に進行するものと推定している。



Scheme 6. Plausible Reaction Mechanism for the Nickel-Catalyzed Intramolecular Four-Component Connection Reaction

本研究では、ニッケル触媒により、ジメチル亜鉛，１，ω－ジエンイン，カルボニル化合物の分子内四成分連結反応が室温で速やかに進行することを見出した。本反応で重要なことは、ニッケル触媒により、一挙にジメチル亜鉛，アルキン，１，３－ジエン，カルボニル化合物の四成分が反応し、新たに３種類の炭素－炭素結合が形成するだけではなく、極めて高い遠隔位１，５－ジアステレオ選択性が発現することである。さらに、ジメチル亜鉛のメチル基がジエン由来の置換基に対して、アルキンにシス付加するため、環外四置換アルケンの立体選択的な合成法として有用性が高い。また五員環化合物のみならず、一般的に合成困難な六員環生成物の合成も可能であり、多彩な置換形式，原子組成を持つ環状化合物の合成に広く応用できる。このような多成分連結を伴う１，５－ジアステレオ選択的な炭素―炭素結合形成反応は極めて稀少であり、医薬品や農薬などの生理活性物質や高機能性材料の炭素骨格構築法としての応用が期待される。

Experimental Section

Reactions employed oven-dried glassware unless otherwise noted. Thin later chromatography (TLC) employed glass 0.25 mm silica gel plates with UV indicater (Merck, Silica gel 60F254). Frash chromatograply columns were 230-400 mash silica gel as a slurry in hexane. Gradient flash chromatography was conducted eluting with a continuous gradient from hexane to the indicated solvent. Distillation were carried out in a Kugelrohr apparatus and boiling points are meant to refer to the oven temperature. Proton and carbon NMR data were obtained with ether a JEOL-GX400, Varian 300, or Gemini 200 with tetramethylsilane as an internal standard Chemical shift values were given in ppm downfield from the internal standard. Infrared spectra were recorded with a JASCO A-100 FT-IR spectrophotometer. High resolution mass spectra were measured with a JEOL JMS-DX303. Combustion analysis were performed by the Instrumental Analysis Center of Nagasaki University. Analysis agreed with the calculated value within ±0.4 %.

Solvent and Reagents. Tetrahydrofuran (THF) and ether were dried and distilled from sodium/benzophenone ketyl immediately prior to use under nitrogen atomosphere. Dichloromethane and triethylamine were distilled over calcium hydride. Dimethylformamide (DMF) and dimethylsulfoxide was dried over calcium sulfate and calcium hydride, respectively, under reduced pressure. Acetone was distilled over potassium carbonate and hexane over sodium. Aldehydes were distilled under reduced pressure prior to use. Dimethyl zinc, diethylzinc, triethylborone (1.0 M in hexane; KANTO CHEMICAL), $Ni(acac)_2$ (Aldrich) were used as received.

General Procedure for the Ni-Catalyzed Cyclization of 1,ω-Dienyne: (run 2, Table 2):

To a homogeneous solution of $Ni(acac)_2$ (25.6 mg, 0.1 mmol) and 1,ω-dienyne **1h** (303 mg, 1 mmol) in dry THF (5 ml) were successively added benzaldehyde (212 mg, 2 mmol) and dimethylzinc (2.4 ml, 1 M in hexane). The mixture was stirred at room temperature for 1 h under N_2. The solution mixture was poured into ice water and 2 M HCl (5 ml) was added, then the mixture was extracted with ethyl acetate (2 x 20 ml). The combined organic extracts were washed with sat. $NaHCO_3$ and with sat. NaCl, dried ($MgSO_4$), and concentrated *in vacuo*. The reside was purified by column chromatography over silica gel (hexane:ethyl acetate = 12:1, v/v) to give **2h** in 96% yield (408 mg). $R_{f(\mathbf{2h})}$ = 0.20 (hexane: ethyl acetate = 4:1, v/v).

Preparation of 1,ω-Dienyne 1

2-(2,4-Pentadienyl)-2-(2-propynyl)malonic Acid Diethyl Ester (**1a**) and **2-(2-Butynyl)-2-(2,4-pentadienyl)malonic Acid Diethyl Ester (1b)**:[15],[16] To a solution of 1,4-pentadien-3-diol (9.73 ml, 100 mmol, Aldrich) was added conc. HCl (25 ml, 300 mmol) at 0 ℃ and the mixture was stirred at the same temperature for 2 h. The mixture was extracted with pentane and the organic layer was successively washed with water and sat. $NaHCO_3$ and dried over $MgSO_4$. After distillation of the solvent under atmospheric pressure, the residue was distilled (70 ℃/100 mmHg) to give the 1-chloro-2,4-pentadiene (75%).

Into a round-bottom flask was placed NaH (1.44 g; a 60% dispersion in oil, 36 mmol). The dispersion was washed hexane (2 x 5 ml). Into the flask were added THF (120 ml) and DMSO (10 ml), and the heterogeneous mixture was cooled to 0 ℃. Into this was added dropwise a solution of diethyl malonate (9.7 ml, 65 mmol/THF 10 ml) at same temperature. After 1 h, a solution of 1-chloro-2,4-pentadiene (3.1 ml, 30 mmol) in THF (10 ml) was added dropwise at the same temperature. The resulting mixture was allowed to warm to ambient temperature, stirred for 16 h. Into this mixture was added water (50 ml). THF was removed *in vacuo* and the resulting oil was dissolved in ether. The organic layer was washed with water dried ($MgSO_4$), and concentrated *in vacuo*. The residue was purified by column chromatography

over silica gel (hexane:ethyl acetate = 64/1, v/v) to provide 2-(2,4-pentadienyl)malonic acid diethyl eater (70%).

In a round-bottom flask was placed NaH (250 mg; a 60% dispersion in oil, 6.25 mmol). The dispersion was washed with hexane as above. Into the flask were THF (30 ml) and DMSO (5 ml). This heterogeneous mixture was cooled to 0 ℃. To this was added dropwise a solution of 2-(2,4-pentadienyl)malonic acid diethyl ester (1.13 g, 5 mmol) in THF (5 ml) at the same temperature. After 1 h, either a solution of propargyl bromide (1.12 ml, 10 mmol) in THF (5 ml) or a solution of 1-bromo-2-butyne (0.88 ml, 10 mmol) in THF (5 ml) was added dropwise. The mixture was allowed to warm to ambient temperature, and stirred for 2 h. After addition water (25 ml), THF was removed *in vacuo* and a resulting oil was partitioned between ether and water. The organic layer was washed with water, dried ($MgSO_4$), and the solvent was removed *in vacuo*. The residue was purified by column chromatography over silica gel (hexane/ethyl acetate = 16/1, v/v) to provide **1a** in 79% yield. Distillation (110 ℃/0.3 mmHg) furnished **1b** in 73% yield. **1a**: IR (neat) 3292 (m), 1736 (s), 1192 (s), 1007 (m) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.25 (t, *J* = 7.0 Hz, 6 H), 2.02 (t, *J* = 2.6 Hz, 1 H), 2.79 (d, *J* = 2.6 Hz, 2 H), 2.83 (br d, *J* = 7.8 Hz, 2 H), 4.21 (q, *J* = 7.0 Hz, 4 H), 5.02 (br d, *J* = 10.6 Hz, 1 H), 5.13 (br d, *J* = 16.5 Hz, 1 H), 5.50 (dt, *J* = 15.2, 7.8 Hz, 1 H), 6.16 (br dd, *J* = 10.6 Hz, 15.2 Hz, 1 H), 6.27 (dt, *J* = 16.5, 10.6 Hz, 1 H). Anal Calcd for $C_{15}H_{20}O_4$: C, 68.16; H, 7.63. Found: C, 68.50; H, 7.43. **1b** is a known compound (RN 222549-37-3): IR (neat) 1738 (s), 1603 (m), 1211 (s), 1055 (s) cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 1.26 (t, *J* = 7.0 Hz, 6 H), 1.77 (t, *J* = 2.0 Hz, 3 H), 2.73 (q, *J* = 2.0 Hz, 2 H), 2.81 (br d, *J* = 8.0 Hz, 2 H), 4.20 (q, *J* = 7.0 Hz, 4 H), 5.02 (br d, *J* = 10.2 Hz, 1 H), 5.13 (br d, *J* = 16.5 Hz, 1 H), 5.52 (dt, *J* = 15.0, 8.0 Hz, 1 H), 6.14 (br dd, *J* = 10.2, 15.0 Hz, 1 H), 6.28 (dt, *J* = 16.5, 10.2 Hz, 1 H).

2-(3-Pentynyl)-2-(2,4-pentadienyl)malonic Acid Dimethyl Ester (**1m**) is prepared from 2-(2,4-pentadienyl)malonic acid diethyl ester (as above) and 1-bromo-3-pentyne (Ardrich) under similar way to give **1a** and **1b**. **1m**: IR (neat) 2955 (s), 1732 (s), 1437 (s), 1271 (s), 1202 (s),

1178 (s), 1084 (m), 1013 (m), 974 (m) cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.75 (s, 3 H), 2.08 – 2.02 (m, 4 H), 2.68 (d, *J* = 7.8 Hz, 2 H), 3.72 (s, 6 H), 5.02 (d, *J* = 10.2 Hz, 1 H), 5.13 (d, *J* = 16.6 Hz, 1 H), 5.49 (dt, *J* = 7.8, 14.9 Hz, 1 H), 6.09 (dd, *J* = 10.2, 14.9 Hz, 1 H), 6.28 (dt, *J* = 16.6, 10.2 Hz, 1 H); HRMS calcd for $C_{15}H_{20}O_4$: 264.1362. Found *m*/*z* (relative intensity): 264.1353 (M^+, 100), 249 (12).

***N*-2-Butynyl-*N*-(*2E*,4-pentadienyl)-*p*-toluenesulfonamide** (**1c**):[17] Into a mixture of *p*-toluenesulfonamide (3.77 g, 22 mmol) and potassium carbonate (2.76 g, 20 mmol) in acetone (20 ml) was added dropwise 1-chloro-2,4-pentadiene (2.1 ml, 20 mmol) at room temperature. The mixture was refluxed for 23 h under N_2 and then poured into water. Extraction with dichloromethane, drying over $MgSO_4$, concentration *in vacuo*, followed by purification by column chromatography over silica gel (hexane/ethyl acetate = 16/1, v/v) provided *N*-(2,4-pentadienyl)-*p*-toluenesulfoamide in 44% isolated yield.

Into a flask containing NaH (400 mg; a 60% dispersion in oil, 10 mmol; washed with hexane as above) was added DMF (50 ml) and then was added dropwise a solution of *N*-(2,4-pentadienyl)-*p*-toluenesulfoamide (1.90 g, 8.0 mmol) in DMF (10 ml) at 0 ℃.

After stirring for 1 h, 1-bromo-2-butyne (1.05 ml, 12 mmol) was added dropwise via syringe. The mixture was allowed to warm to ambient temperature and stirred for 20 h, and then poured into water. Extracts with ethyl acetate were dried over $MgSO_4$ and concentrated *in vacuo* and the residue was purified by column chromatography over silica gel (hexane/ethyl acetate = 16/1, v/v) to provide **1c** in 90% yield. **1c**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.56 (t, *J* = 2.0 Hz, 3 H), 2.42 (s, 3 H), 3.83 (br d, *J* = 8.0 Hz, 2 H), 4.00 (q, *J* = 2.0 Hz, 2 H), 5.11 (br d, *J* = 10.3 Hz, 1 H), 5.20 (br d, *J* = 16.5 Hz, 1 H), 5.58 (dt, *J* = 15.8, 8.0 Hz, 1 H), 6.22 (br dd, *J* = 10.3, 15.0 Hz, 1 H), 6.33 (dt, *J* = 16.5, 10.3 Hz, 1 H), 7.31 (d, *J* = 8.4 Hz, 2 H), 7.72 (d, *J* = 8.4 Hz, 2 H), Anal.Calcd for $C_{16}H_{19}NO_2S$: C, 66.41; H, 6.62; N, 4.84; S, 11.08. Found: C, 66.80; H, 6.82; N, 4.49; S, 11.48.

5-(2-Butynlyoxy)-(1,3*E*)-pentadiene (**1d**) and **1-[(2*E*,4)-Pentadienyloxy]-3-phenyl-2-propyne** (**1e**):[18] Into a flask containing NaH (680 mg; a 60% dispersion in oil, 17 mmol; washed with hexane as above) was added THF (30 ml) and the mixture was cooled to 0 ℃. To this solution of 1-phenyl-1-propyn-1-ol (15 mmol) in 10 ml THF at the same temperature. The resulting mixture was allowed to warm to at room temperature and stirred for 1 h. This mixture was cooled again to 0 ℃, and into this a solution of 1-chloro-2,4-pentdiene (1.79 ml, 17 mmol) in 10 ml THF was added dropwise via syringe. The mixture was poured onto ice-water and extracted with ether. The organic phase was washed with sat. NH_4Cl and with sat. $NaHCO_3$, and dried over $MgSO_4$. The solvent was removed *in vacuo* and the residue was purified by distillation (90℃/5 mmHg) to give **1d** in 73% yield or by column chromatography over silica gel (hexane/ethyl acetate = 16/1, v/v) to provide **1e** in 94% yield. **1d**: IR (neat) 1605 (m), 1074 (s), 1005 (s), 907 (s) cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 1.88 (t, *J* = 2.0 Hz, 3 H), 4.08 (br d, *J* = 7.0 Hz, 2 H), 4.13 (q, *J* = 2.0 Hz, 2 H), 5.12 (br d, *J* = 11.0 Hz, 1 H), 5.22 (br d, *J* = 16.5 Hz, 1 H), 5.78 (br dt, *J* = 15.0, 7.0 Hz, 1 H), 6.27 (br dd, *J* = 11.0, 15.0 Hz, 1 H), 6.36 (dt, *J* = 16.5, 11.0 Hz, 1 H). Anal. Calcd for $C_9H_{12}O$: C, 79.37; H, 8.88. Found: C, 79.08; H, 8.58. **1e** is a known compound (RN 478176-03-3): IR (neat) 1603 (m), 1076 (s), 1005 (s) 756 (s), 691 (s) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 4.19 (d, *J* = 6.0 Hz, 2 H), 4.39 (s, 2 H), 5.14 (br d, *J* = 10.3 Hz, 1 H), 5.24 (br d, *J* = 15.6 Hz, 1 H), 5.81 (br dt, *J* = 12.2, 6.0 Hz, 1 H), 6.33 (dd, *J* = 10.3, 12.2 Hz, 1 H), 6.37 (dt, *J* = 15.6, 10.3 Hz, 1 H), 7.28 – 7.36 (m, 3 H), 7.40 – 7.50 (m, 2 H).

5-(3-Pentynyloxy)-(1,3*E*)-pentadiene (1j) is prepared from 1-chloro-2,4-pentadiene and 3-pentyn-1-ol under similar way to give **1d** and **1e**. **1j**: IR (neat) 3086 (w), 2918 (s), 2858 (s), 1728 (w), 1605 (w), 1439 (m), 1360 (m), 1113 (s), 1005 (m), 970 (m), 908 (w) cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 1.78 (br s, 3 H), 2.42 (br t, *J* = 6.8 Hz, 2 H), 3.52 (t, *J* = 6.8 Hz, 2 H), 4.05 (d, *J* = 6.4 Hz, 2 H), 5.10 (d, *J* = 10.4 Hz, 1 H), 5.22 (d, *J* = 16.6 Hz, 1 H), 5.77 (dt, *J* =

14.9, 6.4 Hz, 1 H), 6.26 (dd, *J* = 10.4, 14.9 Hz, 1H), 6.35 (dt, *J* = 16.6, 10.4 Hz, 1 H); HRMS calcd for $C_{10}H_{14}O$-CH_3: 135.0810. Found *m/z* (relative intensity): 135.0644 (M – CH_3, 100), 122 (18), 105 (20).

2-[(2*E*,4)-Pentadienyl]-2-(3-pentynyl)malonic Acid Diethtyl (**1g**): A solution of 3-pentyn-1-ol (3.0 ml, 33 mmol, Aldrich) and triethylamine (4.6 ml, 33 mmol) in dichlromethane (50 ml) was cooled to 0 ℃. To this solution was added *p*-toluenesulfonyl chloride (5.72 g, 30 mmol) at the same temperature. The resulting mixture was warmed to room temperature and 24 h. The mixture was washed sat. $NaHCO_3$ and with brine. The organic phase was dried over $MgSO_4$ and the solvent was removed *in vacuo*. Distillation of the residue (160 ℃/0.2 mmHg) provided 3-pentynyl tosylate in 86% yield.

NaH (280 mg; a 60% dispersion in oil, 6.9 mmol) placed in a flask was washed with hexane under N_2. To the flask were added THF (30 ml) and DMSO (5 ml) via syringe and the mixture was cooled to 0 ℃. To this mixture was added dropwise a solution of 2-(2,4-pentadienyl)malonic acid diethyl eater (1.2 ml, 5.7 mmol) in THF (10 ml) at the same temperature. After being allowed to warm to room temperature and stirred for 1 h, a solution of 3-pentynyl tosylate (1.64 g, 6.9 mmol) in THF (10 ml) was added dropwise into this mixture. The mixture was heated at reflux for 28 h. Into this mixture was added ice and THF was removed *in vacuo*. The residual oil was partitioned between ether and water. The organic layer was washed with water, dried ($MgSO_4$), and concentrated *in vacuo*. The residue was purified by column chromatography over silica gel (hexane/ethyl acetate = 16/1, v/v) to provide **1g** in 62% yield. **1g**: IR (neat) 1732 (s), 1603 (m), 1188 (s), 1082 (s), 1007 (s) cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 1.25 (t, *J* = 6.8 Hz, 6 H), 1.75 (br s, 3 H), 2.06 – 2.17 (m, 4 H), 2.68 (br d, *J* = 7.6 Hz, 2 H), 4.18 (q, *J* = 6.8 Hz, 4 H), 5.03 (br d, *J* = 10.6 Hz, 1 H), 5.12 (br d, *J* = 16.6 Hz, 1 H), 5.53 (dt, *J* = 15.0, 7.6 Hz, 1 H), 6.10 (br dd, *J* = 10.6, 15.0 Hz, 1 H), 6.27 (br dt, *J* = 16.6, 10.6 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 3.4, 14.0, 14.1, 32.0, 36.0, 57.2,

61.2, 76.0, 77.9, 116.3, 127.7, 134.8, 136.4, 170.5; HRMS calcd for $C_{17}H_{24}O_4$: 292.1675. Found *m/z* (relative intensity): 292.1660 (M^+, 13), 247 (100).

***N*-[(2*E*,4)-Pentadienyl]-*N*-(3-pentynyl)-*p*-toluenesulfonamide** (**1h**): NaH (1.8 g; 60% dispersion in oil, 12 mmol) placed in a flask was washed with hexane under N_2. Into the flask were added THF (50 ml) and DMSO (5 ml) and the mixture was cooled to 0 ℃. To this solution was added dropwise a solution of *N*-(2,4-pentadieneyl)-*p*-toluenesulfonamide (2.37 g, 10 mmol) in THF (10 ml) at the same temperature. This solution was allowed to warm to room temperature and stirred for 1 h and then, into which were added 3-pentynyl tosylate (2.86 g, 12 mmol, dissolved in 10 ml THF) and sodium iodide (0.48 g, 12 mmol). The mixture was refluxed for 43 h and then poured into water. The ethereal extracts were washed with water, dried ($MgSO_4$), and concentrated *in vacuo*. The residue was purified by column chromatography over silica gel (hexane/ethyl acetate = 16/1, v/v) to provide **1h** in 45% yield. **1h**: ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.74 (t, *J* = 3.0 Hz, 3 H), 2.38 (tq, *J* = 8.0, 3.0 Hz, 2 H), 2.42 (s, 3 H), 3.23 (t, *J* = 8.0 Hz, 2 H), 3.87 (d, *J* = 7.0 Hz, 2 H), 5.08 (br d, *J* = 10.0 Hz, 1 H), 5.17 (br d, *J* = 16.6, 10.0 Hz, 1 H), 7.29 (d, *J* = 8.4 Hz, 2 H), 7.71 (d, *J* = 8.4 Hz, 2 H), HRMS calcd for $C_{17}H_{21}NO_2S$: 303.1293. Found *m/z* (relative intensity): 303.1284 (M^+, 4), 250 (100), 212 (13).

***N*-[(3*E*,5)-hexadienyl]-*N*-(2-butynyl)-*p*-toluenesulfonamide** (**1i**):[19],[20] Into a mixture of *p*-toluenesulfonamide (6.85 g, 40 mmol) and potassium carbonate (2.76 g, 20 mmol) in acetone (20 ml) was added dropwise propergyl bromide (1.8 ml, 20 mmol) at room temperature and the mixture was refluxed for 21 h. The mixture was poured into water and extracted with ether. The organic extact was dried ($MgSO_4$) and concentrated *in vacuo*. The residue was purified by column chromatography over silica gel (hexane/ethyl acetate = 16/1, v/v) to provide *N*-(2-butynyl)-*p*-toluenesulfonamide in 35% yield.

A solution of lithium diisopropylamide (LDA) was prepared by the slow addition of *n*-BuLi (60 ml, 96 mmol, 1.6 M in hexane) to a solution of diisopropylamine (13.5 ml, 96 mmol) in THF (160 ml) at –78 ℃. To this solution was added dropwise hexamethylphosphotriamide (18.1 ml, 104 mmol). After stirring at –78 ℃ for 30 min, methyl sorbate (10.5 ml, 80 mmol) was added over 2 h and stirring was continued for an additional hour at –78 ℃. Then the dark-red mixture was siphoned into rapidly stirred solution of acetic acid (13.7 ml, 240 mmol) in H_2O (288 ml) at 0 ℃. The resultant solution was extracted with pentane. The combined extracts were washed with water and then with sat. $NaHCO_3$. The organic phase was dried over $MgSO_4$ and the solvent removed *in vacuo*. The residue was distilled (80 ℃/20 mmHg) to give methyl 3,5-hexadienoate in 99% yield.

A solution of methyl 3,5-hexanoate (3.79 g. 30 mmol) in ether (10 ml) was added into suspension of $LiAlH_4$ (910.8 mg, 24 mmol) in ether (50 ml) at 0 ℃. After being stirred for 1 h at same temperature, the mixture was quenched by addition of a mixture of THF/H_2O (2:1, 30 ml), and then 2M HCl (30 ml). The mixture was extracted with ethyl acetate and the combined extracts were washed with brine, dried ($MgSO_4$), and concentrated *in vacuo*. The residue was distilled (80 ℃/10 mmHg) to give 3,5-hexadien-1-ol in 78% yield.

N-(2-butynyl)-*p*-toluenesulfonamide (1.56 g, 7 mmol) and triphenylphosphine (3.67 g, 14 mmol) were dissolved in THF (20 ml). To this solution were added dropwise 3,5-hexadiene-1-ol (0.59 g, 6 mmol) and diethyl azodicarboxylate (2.09 g, 12 mmol, 40% in toluene) at room temperature, and the mixture was stirred for 4 h. The solvents were removed *in vacuo* and the residue was purified by column chromatography over silica gel (hexane/ethyl acetate = 16/1, v/v) to provide **1i** in 63% yield. **1i**: ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.56 (t, *J* = 3.0 Hz, 3 H), 2.36 (q, *J* = 7.0 Hz, 2 H), 2.41 (s, 3 H), 3.20 (t, *J* = 7.0 Hz, 2 H), 4.04 (q, *J* = 3.0 Hz, 2 H), 5.02 (br d, *J* = 10.0 Hz, 1 H), 5.12 (br d, *J* = 15.8 Hz, 1 H), 5.62 (dt, *J* = 15.8, 7.0 Hz, 1 H), 6.12 (br dd, *J* = 10.0, 15.8 Hz, 1 H), 6.29 (dt, *J* = 15.8, 10.0 Hz, 1 H), 7.29 (d, *J* = 8.5 Hz, 2 H), 7.72 (d, *J* = 8.5 Hz, 2 H). Anal. Calcd for $C_{17}H_{21}NO_2S$: C, 67.29; H, 6.98; N, 4.62; S, 10.57.

Found: C, 67.65; H, 6.60; N, 4.48; S, 10.97.

***o*-[(2*E*,4-Pentadienyloxy)(trimethylsilylethynyl)benzene** (**1k**): and ***o*-[(2*E*,4)-Pentadienyloxy](phenylethynyl)benzene** (**1l**):[21],[22] Into a mixture of bis-(triphenylphosphine)palladium(II) dichloride (221 mg, 0.3 mmol) and copper(I) iodide (171.4 mg, 0.9 mmol) in benzene (50 ml) was added 2-iodophenol (2.2 g., 10 mmol), either ethynyltrimethylsilane (2.1 ml, 15 mmol) or ethynyl benzene (1.6 ml, 15 mmol), and diisopropylamine (1.4 ml, 10 mmol). The resulting solution was stirred at room temperature for 2 h. The mixture was passed through a short pad of celite and the solvent was removed *in vacuo*. The residue was dissolved in ethyl acetate and the solution was washed water, dried ($MgSO_4$), and concentrated *in vacuo*. The residue was purified by column chromatography over silica gel (hexane/ethyl acetate = 16/1, v/v) to provide either *o*-(trimethylsilylethynyl)phenol in 99% yield or *o*-phenylethynylphenol in 99% yield.

Into a mixture of *o*-(trimethylsilylethynyl)phenol (1.93 g, 10 mmol) and potassium carbonate (1.52 g, 11 mmol) in acetone (30 ml) were added potassium iodide (0.17 g, 1 mmol) in one portion and 1-chloro-2,4-pentadiene (1.2 ml, 11 mmol) dropwise at room temperature. The mixture was refluxed for 5 h. After being passed through a short pad of celite, washed with ethyl acetate, the filtrate was concentrated *in vacuo*. The residue was dissolved in ether and solution was washed with sat. $NaHCO_3$ and with brine, dried ($MgSO_4$), and concentrated *in vacuo*. The residue was purified by column chromatography over silica gel (hexane/ethyl acetate = 16/1, v/v) to provide **1k** in 53% yield. Alkylation of 2-phenylethynylphenol (1.94 g, 10 mmol) with 1-chloro-2,4-pentadiene was undertaken in a similar way to give **1l** in 86% yield. **1k**: IR (neat) 2458 (s), 1595 (s), 1114 (s), 1005 (s), 842 (s), 750 (s) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.26 (s, 9 H), 4.64 (d, *J* = 5.0 Hz, 2 H), 5.13 (br d, *J* = 10.6 Hz, 1 H), 5.25 (br d, *J* = 16.6 Hz, 1 H), 5.92 (dt, *J* = 15.0, 5.0 Hz, 1 H), 6.37 (br dd, *J* = 10.6, 15.0 Hz, 1 H), 6.48 (br dt, *J* = 16.6, 10.6 Hz, 1 H), 6.85 (br d, *J* = 8.0 Hz, 1 H), 6.89 (br t, *J* = 8.0 Hz, 1 H), 7.26

(br t, *J* = 8.0 Hz, 1 H), 7.45 (br d, *J* = 8.0 Hz, 1 H); HRMS calcd for $C_{16}H_{20}OSi$: 256.1283. Found *m/z* (relative intensity): 256.1273 (M^+, 100), 242 (18), 241 (80). **1l**: IR (neat) 1593 (s), 1107 (s), 1003 (s), 754 (s), 691 (s) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 4.68 (d, *J* = 5.0 Hz, 2 H), 5.12 (br d, *J* = 10.0 Hz, 1 H), 5.20 (br d, *J* = 16.4 Hz, 1 H), 5.96 (dt, *J* = 14.6, 5.0 Hz, 1 H), 6.37 (br dd, *J* = 10.0, 14.6 Hz, 1 H), 6.48 (br dt, *J* = 16.4, 10.0 Hz, 1 H), 6.89 (d, *J* = 8.0 Hz, 1 H), 6.96 (t, *J* = 8.0 Hz, 1 H), 7.20 – 7.45 (m, 4 H), 7.46 – 7.63 (m, 3 H); HRMS calcd for $C_{19}H_{16}O$: 260.1201. Found for (relative intensity): 260.1204 (M^+, 100), 259 (49), 246 (6), 233 (15).

3-Hydroxy-1,4,4-triphenyl-(6*E*,8)-nonadiene-1-yne (**1f**):[23] Into a mixture of palladium(II) acetate (68 mg, 0.3 mmol), 1,1'-bis(diphenylphosphino)ferrocene (166 mg, 0.3 mmol) and lithium chloride (250 mg, 6 mmol) in THF (30 ml) were added 1,4-pentadiene-3-ol (0.58 ml, 6 mmol), diphenylacetaldehyde (0.89 ml, 5 mmol, Aldrich), triethylamine (0.84 ml, 6 ml), and triethylborane (12 ml, 12 mmol, 1 M in hexane) via syringe under nitrogen atmosphere. The resulting solution was stirred at 50 ℃ for 24 h. After the reaction completes, the most portion of the solvents was removed with a rotary evaporator, and the residual solution is diluted with ethyl acetate (30 ml). The organic phase is washed with 2 M HCl (20 ml), sat. $NaHCO_3$ (30 ml), and brine (30 ml), and then dried over magnesium sulfate, filtered, and concentrated. The residue is purified by means of flash column chromatography over silica gel (eluent; hexane/ethyl acetate = 16/1, v/v) to provide 2,2-diphenyl-(4*E*,6)-heptadienal in 92% yield.

A solution of lithium acetylide was prepared by the addition of *n*-BuLi (2 ml, 3.3 mmol, 1.6 M in hexane) to a solution of phenylacetylene (0.36 ml, 3.3 mmol) in THF (5 ml) at –78 ℃. A solution of 2,2-diphenyl-(4*E*,6)-heptadienal (787 mg, 3 mmol) dissolved in THF (5 ml) was added dropwise to the lithium acetylide solution at –78 ℃, and the reaction mixture was stirred at ambient temperature for 3 h. The mixture was quenched by the addition of 1 M HCl

(4 ml) at 0 ℃ and diluted with diethyl ether (25 ml). The organic phase was washed with 1 M HCl (25 ml), sat. $NaHCO_3$ (25 ml), and brine (25 ml), and then dried over magnesium sulfate, filtered, and concentrated. The residue is purified by means of flash column chromatography over silica gel (hexane/ethyl acetate = 16/1, v/v) to provide **1f** in 69% yield. **1f**: IR (neat) 3422 (s), 3057 (s), 2926 (m), 2199 (w), 1663 (w), 1595 (m), 1495 (m), 1445 (m), 1034 (m), 762 (s), 698 (s) cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 3.15 (d, *J* = 7.7 Hz, 2 H), 4.95 (d, *J* = 10.6 Hz, 1 H), 5.07 (d, *J* = 16.4 Hz, 1 H), 6.13 (dd, *J* = 10.6, 14.9 Hz, 1 H), 6.17 (dt, *J* = 16.4, 10.6 Hz, 1 H), 7.30 (m, 15 H); HRMS calcd for $C_{27}H_{24}O$: 364.1827. Found *m/z* (relative intensity): 364.1809 (M^+, 100), 347 (5), 346 (15).

7-(2-Butynyl)-6,6-diphenyl-(1,3*E*)-heptadiene (**1n**): To a solution of 2,2-diphenyl-(4*E*,6)-heptadienal (2.62 g, 10 mmol) dissolved in ethanol (50 ml) was added $NaBH_4$ (0.38 g, 10 mmol) and the mixture was stirred at room temperature for 16 h. The solvent was removed *in vacuo* and the residue was dissolved in diethyl ether (50 ml). The solution was washed with 2 M HCl (30 ml), and then the aqueous phase was extracted with diethyl ether (3 x 30 ml). Combined organic extracts was washed with sat. $NaHCO_3$ (25 ml), and brine (30 ml), and then dried over magnesium sulfate, filtered, and concentrated. The residue is purified by means of flash column chromatography over silica gel (hexane/ethyl acetate = 16/1, v/v) to provide 2,2-diphenyl-(4*E*,6)-heptadiene-1-ol in 88% yield.

Into a flask containing NaH (420 mg; a 60% dispersion in oil, 10 mmol; washed with hexane) was added DMF (20 ml) and the mixture was cooled to 0 ℃. To this solution was dropwise a solution of 2,2-diphenyl-(4*E*,6)-heptadiene-1-ol (2.31 g, 8.7 mmol) in 5 ml DMF at the same temperature. The resulting mixture was allowed to warm at room temperature and stirred for 3 h. This mixture was cooled again to 0 ℃, and into this a solution of 1-bromo-2-butyne (0.85 ml, 9.6 mmol, Ardrich) in 5 ml DMF was added dropwise via syringe. The

mixture was allowed to warm to ambient temperature, and stirred for 24 h. The mixture was poured onto ice-water 30 ml and extracted with pentane 30 ml. The organic phase was washed with sat. NH_4Cl and with sat. $NaHCO_3$, and dried over $MgSO_4$. The solvent was removed *in vacuo* and the residue was purified by column chromatography over silica gel (hexane/ethyl acetate = 16/1, v/v) to provide **1n** in 27% yield. **1n**: IR (neat) 3057 (w), 2918 (m), 2243 (w), 1712 (s), 1599 (w), 1495 (m), 1447 (s), 1360 (m), 1259 (m), 1090 (s), 1028 (m), 758 (s), 700 (s) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.83 (br s, 3 H), 3.02 (d, *J* = 7.4 Hz, 2 H), 4.00 – 4.06 (m, 4 H), 4.93 (d, *J* = 10.2 Hz, 1 H), 5.06 (d, *J* = 16.7 Hz, 1 H), 5.39 (dt, *J* = 14.6, 7.4 Hz, 1 H), 6.10 (dd, *J* = 10.2, 14.6 Hz, 1 H), 6.20 (dt, *J* = 16.7, 10.2 Hz, 1 H), 7.13 – 7.43 (m, 10 H); HRMS calcd for $C_{23}H_{24}O$: 316.1827. Found *m/z* (relative intensity): 316.1825 (M^+, 2), 264 (6), 249 (100).

(2*S,4'*S**)-4,4-Diethoxycarbonyl-2-[4-hydroxy-4-phenyl-(1*E*)-butenyl]-(1*Z*)-ethylidenecyclopentane** (**2a**): a mixture of two diastereomers in a ratio of 11:1; IR (neat): 3530 (s), 1724 (s), 1157 (s), 970 (s), 912 (s), 700 (s) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, major isomer) δ 1,23 (t, *J* = 7.1 Hz, 3 H), 1.24 (t, *J* = 7.1 Hz, 3 H), 1.53 (ddm, *J* = 2.4, 7.1 Hz, 3 H), 1.98 (dd, *J* = 6.6, 13.2 Hz, 1 H), 2.20 (d, *J* = 2.9 Hz, 1 H), 2.40 (ddd, *J* = 6.6, 7.7, 13.6 Hz, 1 H), 2.47 (br dt, *J* = 13.6, 5.0 Hz, 1 H), 2.64 (ddd, *J* = 1.5, 8.4, 13.2 Hz, 1 H), 2.77 (br d, *J* = 15.8 Hz, 1 H), 3.01 (dq, *J* = 15.8, 2.4 Hz, 1 H), 3.35 (br dd, *J* = 6.6, 8.4 Hz, 1 H), 4.17 (q, *J* = 7.1 Hz, 2 H), 4.18 (q, *J* = 7.1 Hz, 2 H), 4.68 (ddd, *J* = 2.9, 4.8, 7.7 Hz, 1 H), 5.41 (ddd, *J* = 5.0. 6.6, 15.2 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$, major isomer) δ 14.1, 14.2, 40.9, 41.5, 42.6, 42.7, 59.1, 61.4, 61.5, 73.6, 119.1, 125.5, 125.8, 127.4, 128.4, 136.0, 140.6, 144.0, 171.6, 171.9; HMMS calcd for $C_{23}H_{30}O_5$: 386.2093. Found *m/z* (relative intensity): 386.2104 (M^+, 2), 368 (38), 280 (81), 206 (100), 117 (16).

(2*S,4'*S**)-4,4-diethoxycarbonyl-2-[4-hydroxy-4-phenyl-(1*E*)-butenyl]-1-**

isopropylidenecyclopentane (**2b**): a mixture of two diastereomers in a ratio of 8:1; IR (neat) 3466 (s), 1732 (s), 1252 (s), 1194 (s), 972 (m), 702 (s) cm^{-1}; ^{1} H NMR (300 MHz, $CDCl_3$, major isomer) δ 1.23 (t, *J* = 7.1 Hz, 3 H), 1.24 (t, *J* = 7.1 Hz, 3 H), 1.57 (s, 3 H), 1.66 (s, 3 H), 2.09 (dd, *J* = 5.1, 13.2 Hz, 1 H), 2.28 (d, *J* = 2.9 Hz, 1 H), 2.37 (dt, *J* = 13.9, 8.1 Hz, 1 H), 2.44 (br dt, *J* = 13.9, 4.8 Hz, 1 H), 2.57 (dd, *J* = 8.4, 13.2 Hz, 1 H), 2.83 (d, *J* = 16.7 Hz, 1 H), 2.96 (d, *J* = 16.7 Hz, 1 H), 3.33 (br dd, *J* = 5.1, 8.4 Hz, 1 H), 4.16 (q, *J* = 7.1 Hz, 2 H), 4.19 (q, *J* = 7.1 Hz, 2 H), 4.67 (ddd, *J* = 2.9, 4.8, 8.1 Hz, 1 H), 5.32 (dddm, *J* = 4.8, 8.1, 15.4 Hz, 1 H), 5.42 (dd, *J* = 6.2, 15.4 Hz, 1 H), 7.24 – 7.37 (m, 5 H); ^{13}C NMR (100 MHz, $CDCl_3$, major isomer) δ 14.1, 20.9, 21.5, 38.4, 40.8, 43.0, 44.1, 59.4, 61.4, 61.6, 73.5, 125.4, 125.8, 126.1, 127.3, 128.3, 133.1, 136.7,. 144.1, 171.9, 172.3; HRMS calcd for $C_{24}H_{32}O_5$: 400.2550. Found *m*/*z* (relative intensity): 400.2229 (M^+, 2), 382 (31), 220 (40), 178 (65), 105 (100).

(4*S,4'*S*)-3-Isopropylidene-4-[4-hydroxy-4-phenyl-(1*E*)-butenyl]-*N*-(*p*-toluenesulfonyl)pyrrolidine** (**2c**): IR (neat) 3524 (s), 1597 (m), 1344 (s), 1159 (s), 1045 (s), 970 (m), 760 (m), 655 (s) cm^{-1}; ^{1}H NMR (400 MHz, C_6D_6) δ 1.19 (br s, 3 H), 1.30 (br s, 3 H), 1.89 (s, 3 H), 2.24 (br ddd, *J* = 5.9, 7.3, 13.6 Hz, 1 H), 2.30 (br dt, *J* = 13.6, 7.3 Hz, 1 H), 2.85 (dddm, *J* = 2.2, 6.8, 7.3 Hz, 1 H), 2.96 (dd, *J* = 6.8, 9.3 Hz, 1 H), 3.29 (dd, *J* = 2.2, 9.3 Hz, 1 H), 3.60 (br d, *J* = 13.8 Hz, 1 H), 3.96 (d, *J* = 13.8 Hz, 1 H), 4.42 (ddm, *J* = 5.9, 7.3 Hz, 1 H), 5.17 (dd, *J* = 7.3, 15.2 Hz, 1 H), 5.27 (br dt, *J* = 15.2, 7.3 Hz, 1 H), 6.81 (d, *J* = 8.2 Hz, 2 H), 7.09 – 7.27 (m, 5 H), 7.76 (d, *J* = 8.2 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.5, 21.2, 21.6, 42.4, 44.1, 50.4, 54.2, 73.7, 125.9, 126.1, 126.5, 127.6, 128.0, 128.4, 129.7, 130.0, 132.6, 133.6, 143.6, 143.6, 143.9; HRMS calcd for $C_{24}H_{28}O_2NS$: 394.1814. Found *m*/*z* (relative intensity): 394.1814 (M^+-OH, 10), 262 (54), 138 (82), 121 (51), 91 (100).

(4*S,4*S*'*)-3-Isopropylidene-4-[4-hydroxy-4-phenyl-(1*E*)-butenyl]tetrahydrofuran** (**2d**): IR (neat) 3422 (s), 1053 (s), 970 (m), 700 (s)cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.58 (s, 3 H),

1.64 (s, 3 H), 2.04 (br s, 1 H), 2.46 (ddd, *J* = 2.9, 5.9, 7.7 Hz, 2 H), 3.29 (m, 1 H), 3.71 (dd, *J* = 2.9, 8.6 Hz, 1 H), 3.85 (dd, *J* = 5.9, 8.6 Hz, 1 H), 4.23 (br d, *J* = 12.5 Hz, 1 H), 4.32 (br d, *J* = 12.5 Hz, 1 H), 4.69 (dd, *J* = 5.9, 7.7 Hz, 1 H), 5.41 (br d, *J* = 15.4, 7.7 Hz, 1 H), 5.52 (dd, *J* = 7.7, 15.4 Hz, 1 H), 7.24 – 7.37 (m, 5 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.9, 21.2, 42.5, 45.7 ,70.2, 73.6, 74.6, 123.7, 125.6, 125.9, 127.5, 128.4, 134.0, 134.6, 144.0; HRMS calcd for $C_{17}H_{22}O_2$: 258.1620. Found *m/z* (relative intensity): 258.1620 (M^+, 8), 240 (8), 107 (100), 95 (15), 77 (24).

(4*S,4'*S**)-3-[(1*Z*)-Phenylethylidene]-4-[4-hydroxy-4-phenyl-(1*E*)-butenyl]tetrahydrofuran** (**2e**): a mixture of two diastereomers in a ratio of 8:1; IR (neat) 3404 (s), 1599 (m), 1034 (s), 972 (s), 764 (s), 700 (s) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, major isomer) δ 1.99 (br s, 3 H), 2.20 (d, *J* = 2.3 Hz, 1H), 2.54 (br t, *J* = 6.4 Hz, 2 H), 3.46 (br dt, *J* = 3.9, 6.6 Hz, 1 H), 3.69 (dd, *J* = 3.9, 8.4 Hz, 1 H), 3.96 (dd, *J* = 6.6, 8.4 Hz, 1 H), 4.11 (br d, *J* = 13.2 Hz, 1 H), 4.30 (br d, *J* = 13.2 Hz, 1 H), 4.73 (br dt, *J* = 2.3, 6.4 Hz, 1 H), 5.53 (br dt, *J* = 15.4, 6.4 Hz, 1 H), 5.59 (dd, *J* = 6.6, 15.4 Hz, 1 H), 7.10 – 7.37 (m, 10 H); ^{1}H NMR (400 MHz, $CDCl_3$, minor isomer) δ 1.96 (br s, 3 H), 2.16 (br s, 1 H), 2.52 (t, *J* = 6.4 Hz, 2 H), 3.47 (br dt, *J* = 3.9, 6.6 Hz, 1 H), 3.70 (dd, *J* = 3.9, 8.4 Hz, 1 H), 3.94 (dd, *J* = 6.6, 8.4 Hz, 1 H), 4.11 (br d, *J* = 13.2 Hz, 1 H), 4.29 (br d, *J* = 13.2 Hz, 1 H), 4.73 (br t, *J* = 6.4 Hz, 1 H), 5.52 (br dt, *J* = 15.4, 6.4 Hz, 1 H), 5.58 (dd, *J* = 6.6, 15.4 Hz, 1 H), 7.10 – 7.37 (m, 10 H); ^{13}C NMR (400 MHz, $CDCl_3$, minor isomer) δ 20.8, 42.4, 46.2, 70.6, 73.8, 74.2, 125.9, 126.5, 126.8, 127.1, 127.6, 128.2, 128.2, 128.4, 129.5, 133.7, 137.5, 143.3, 143.9; HRMS calcd for $C_{22}H_{24}O_2NS$: 320.1776. Found *m/z* (relative intensity): 320.1791 (M^+, 27), 147 (15), 105 (100), 95 (25), 78 (17).

Structure Confirmation of the Minor Isomer of 2e; 1) Oxidation of 2e with PCC: A solution of **2e** (8:1 ratio) (288 mg, 0.9 mmol) in dichloromethane (5 ml) was added into a

solution of PCC (646 mg, 3 mmol) in dichloromethane (5 ml) under N_2 at 0 ℃ and the mixture was stirred for additional 2 h at the same temperature. The reaction mixture was diluted with 10 ml of ether and filtered with suction through a celite pad on a glass filer. The filter cake was washed with ether several times. The combined organic extracts were washed with 2 M HCl (5 ml), sat. $NaHCO_3$ (5 ml), and sat. NaCl (10 ml) and dried ($MgSO_4$). The solvent was removed *in vacuo* and the residue was purified by column chromatography over silica gel (hexane/ethyl acetate = 12/1, v/v) to give a ketone as a single isomer in 48% yield. **3-[(1*Z*)-Phenylethylidene]-4-[4-oxo-4-phenyl-(1*E*)-butenyl]tetrahydrofuran**: IR (neat) 1648 (s), 1209 (s), 1036 (s), 935 (m), 700 (s) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 2.00 (s, 3 H), 3.56 (br ddd, *J* = 3.2, 6.5, 7.5 Hz, 1 H), 3.75 (dd, *J* = 3.2, 8.9 Hz, 1 H), 3.78 (br d, *J* = 6.5 Hz, 2 H), 4.02 (dd, *J* = 6.5, 8.9 Hz, 1 H), 4.14 (br d, *J* = 13.0 Hz, 1 H), 4.35 (br d, *J* = 13.0 Hz, 1 H), 5.65 (br dd, *J* = 7.5, 15.3 Hz, 1 H), 5.86 (br dt, *J* = 15.3, 6.5 Hz, 1 H), 7.11 – 7.62 (m, 8 H), 7.92 – 8.02 (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.7, 42.3, 46.4, 70.7, 74.1, 123.5, 126.8, 127.1, 128.2, 128.3, 128.7, 129.8, 133.1, 133.8, 136.7, 137.2, 143.5, 198.2. HRMS calcd for $C_{22}H_{22}O_2$: 318.1620. Found *m/z* (relative intensity): 318.1630 (M^+, 100), 288 (15). **2) Reduction of the ketone with $NaBH_4$**: To a solution of 3-[(1*Z*)-phenylethylidene]-4-[4-oxo-4-phenyl-(1*E*)-butenyl] tetrahydrofuran (0.4 mmol) dissolved in MeOH (2 ml) was added $NaBH_4$ (30 mg, 0.8 mmol) and the mixture was stirred at room temperature for 2 h. The solvent was removed *in vacuo* and the residue was dissolved in ethyl acetate (10 ml). The solution was washed with 2M HCl (5 ml), sat. $NaHCO_3$ (5 ml), sat. NaCl (5 ml), and dried ($MgSO_4$), and concentrated *in vacuo*. The residue was purified by column chromatography over silica gel (hexane/ethyl acetate = 8:1, v/v) to provide a mixture of **2e** in 1:1 ratio in 80% yield.

(3S*,4'S*)-3-[4-Hydroxy-4-phenyl-(1*E*)-butenyl]-5,5-diphenyl-2-[(1Z)-phenylethylidene]cyclopentanol (**2f**): a mixture of two diastereomers in a ratio of 4:1; mp

67.0 – 68.0 ℃ (hexane-dichloromethane); IR (KBr disk) 3356 (s), 3057 (s), 2928 (s), 1684 (m), 1599 (s), 1493 (s), 1447 (s), 1269 (m), 972 (s), 912 (m), 756 (s), 700 (s) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, major isomer) δ 1.89 (s, 3 H), 2.52 (t, *J* = 7.1 Hz, 2 H), 2.64 (dd, *J* = 7.7 12.1 Hz, 1 H), 2.74 (dd, *J* = 9.5, 12.1 Hz, 1 H), 3.13 (br q, *J* = 8.4 Hz, 1 H), 4.71 (t, *J* = 7.1 Hz, 1 H), 4.76 (s, 1 H), 5.47 (dt, *J* = 15.1, 7.1 Hz, 1 H), 5.71 (dd, *J* = 8.4, 15.1 Hz, 1 H), 6.99 – 7.46 (m, 20 H); ^{13}C NMR (100 MHz, $CDCl_3$, major isomer) δ 22.7, 31.6, 42.5, 43.1, 59.0, 73.8, 78.8, 125.4, 125.9, 126.4, 126.9, 127.2, 127.5, 127.8, 128.0, 128.2, 128.4, 128.7, 137.4, 137.8, 140.2, 143.7, 144.0, 144.3, 145.8; HRMS calcd for $C_{35}H_{34}O_2$–H_2O: 468.2403. Found *m/z* (relative intensity): 468.2476 (M^+-H_2O, 100), 107 (61), 77 (57).

(2S*,4'S*)-4,4-Diethoxycaboxy-2-[4-hydro-4-phenyl-(1*E*)-butenyl]-*N*-(p-toluenesulfonyl)piperidine (**2g**): a mixture of two diastereomers in a ratio of 8:1; IR (neat) 3468 (m), 2928 (m), 1732 (s), 1435 (m), 1242 (s), 1200 (m), 1051 (w), 700 (m) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.51 (m, 2 H), 1.60 (br s, 3 H), 2.01 (dd, *J* = 3.3, 9.5 Hz, 1 H), 2.33 (dd, *J* = 8.8, 13.7 Hz, 1 H), 2.17 (dd, *J* = 6.2, 13.9 Hz, 2 H), 2.25 (m, 2 H), 2.36 (m, 1 H), 2.40 (dt, *J* = 13.9, 2.7 Hz, 1 H) , 2.49 (br dt, *J* = 14.3, 3.8 Hz, 1 H), 2.68 (ddd, *J* = 7.3, 9.2, 13.7 Hz, 1 H), 2.80 (ddd, *J* = 5.9, 9.2, 13.7 Hz, 1 H), 3.47 (m, 1 H), 3.59 (m, 1 H), 3.68 (s, 3 H), 5.17 (dddd, *J* = 2.6, 5.9, 8.8, 15.4 Hz, 1 H), 5.41 (br dd, *J* = 4.2, 15.4 Hz, 1 H), 7.15 – 7.32 (m, 5 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.9, 20.1, 22.4, 31.4, 32.1, 35.8, 38.4, 41.3, 52.5, 70.2, 125.4, 125.8, 126.3, 128.4, 128.5, 135.2, 142.4, 172.8, (minor) 36.1, 40.7, 125.3, 135.5; HRMS calcd for $C_{25}H_{34}O_5$: 414.2406. Found *m/z* (relative intensity): 415 (M^++1, 44), 414.2408 (M^+, 84), 396 (M^+-H_2O), 242 (100), 105 (33). Anal. calcd for $C_{25}H_{34}O_5$: C, 72.43; H, 8.27. Found: C, 72.44, 8.29.

(3S*,4'S*)-4-Isopropylidene-3-[4-hydroxy-4-phenyl-(1*E*)-butenyl]-*N*-(p-toluenesulfonyl)piperidine (**2h**): mp 92.0 – 93.0 ℃ (hexane – dichloromethane); IR (KBr

disk) 3460 (m), 1340 (s), 1169 (s), 1103 (m), 932 (m) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.61 (s, 6 H), 2.08 – 2.24 (m, 2 H), 2.32 (dd, *J* = 3.7, 11.4 Hz, 1 H), 2.40 (s, 3 H), 2.43 – 2.51 (m, 3 H), 3.37 (m, 1 H), 3.76 (m, 1 H), 3.78 (dm, *J* = 11.4 Hz, 1 H), 4.73 (br dd, *J* = 5.5, 7.0 Hz, 1 H), 5.50 (ddt, *J* = 1.5, 15.6, 7.1 Hz, 1 H), 5.67 (br dd, *J* = 5.7, 15.6 Hz, 1 H), 7.24 – 7.36 (m, 5 H), 7.30 (d, *J* = 8.2 Hz, 1 H), 7.62 (d, *J* = 8.2 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.9, 20.1, 21.5, 25.4, 39.8, 42.7, 47.1, 51.1, 73.7, 125.9, 126.8, 127.2, 127.4, 127.7, 128.4, 129.6, 133.4, 134.0, 143.3, 144.1; HRMS calcd for $C_{25}H_{31}O_3NS$: 425.2025. Found *m/z* (relative intensity): 425.2042 (M^+, 1), 407 (2), 319 (100), 278 (17).

(4S*,4'S*)-3-Isopropyridene-4-[4-hydroxy-4-phenyl-(1*E*)-butenyl]-*N*-(p-toluenesulfonyl)piperidine (**2i**): IR (neat) 3445 (s), 2856 (s), 1599 (s), 1495 (s), 1454 (s), 1159 (s), 1043 (s), 916 (s), 816 (s), 744 (s), 702 (s), 658 (s) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.62 (d, *J* = 1.5 Hz, 3 H), 1.74 (s, 3 H), 1.77 – 1.86 (m, 2 H), 2.37 (tm, *J* = 6.8 Hz, 1 H), 2.42 (s, 3 H), 2.43 (tm, *J* = 6.8 Hz, 1 H), 2.59 (dt, *J* = 2.9, 12.1 Hz, 1 H), 2.90 (d, *J* = 13.6 Hz, 1 H), 3.36 (m, 1 H), 3.52 (dm, *J* = 12.1 Hz, 1 H), 4.41 (d, *J* = 13.6 Hz, 1 H), 4.58 (tm, *J* = 6.6 Hz, 1 H), 5.20 (ddt, *J* = 1.8, 15.4, 7.0 Hz, 1 H), 5.31 (dd, *J* = 5.1, 15.4 Hz, 1 H), 7.21 – 7.33 (m, 7 H), 7.66 (dt, *J* = 8.1, 2.0 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.0, 20.2, 21.5, 30.3, 37.2, 42.1, 42.5, 44.3, 73.7, 125.8, 126.5, 127.5, 127.7, 128.3, 128.5, 129.6, 134.3, 134.5, 143.3, 143.9; HRMS calcd for $C_{25}H_{31}NO_3S$: 425.2025, Found *m/z* (relative intensity) 425.2014 (M^+, 51), 424 (47), 410 (68), 407 (100).

(2S*,4'S*)-3-Isopropylidene-2-[4-hydroxy-4-phenyl-(1*E*)-butenyl]tetrahydrofuran (**2j**): IR (neat) 3422 (m), 3028 (w), 2955 (s), 1740 (m), 1452 (m), 1240 (m), 1105 (s), 1047 (s), 700 (s) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.65 (br s, 3 H), 1.67 (br s, 3 H), 2.18 (br s, 1 H), 2.22 (br d, *J* =14.5 Hz, 1 H), 2.35 (br d, *J* = 14.5 Hz, 1 H), 2.45 (dm, *J* = 5.3 Hz, 1 H), 2.49 (dm, *J* = 7.0 Hz, 1 H), 3.17 (br s, 1 H), 3.28 (dm, *J* = 10.6 Hz, 1 H), 3.48 (br d, *J* = 11.0 Hz, 1 H),

3.91 (br d, *J* = 11.0 Hz, 1 H), 3.97 (dm, *J* = 10.6 Hz, 1 H), 4.69 (dd, *J* = 5.3, 7.0 Hz, 1 H), 5.43 (br dt, *J* = 15.4, 7.1 Hz, 1 H), 5.75 (br dt, *J* = 15.4, 6.0 Hz, 1 H), 7.23 – 7.37 (m, 5 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.5, 19.8, 27.1, 41.8, 42.8, 68.7, 72.7, 73.6, 124.7, 125.8, 127.3, 127.5, 128.3, 135.1, 144.1; Anal. Calcd for $C_{18}H_{24}O_2$: C, 79.37; H, 8.88. Found: C, 79.20; H, 8.84.

(3S*,4'S*)-3-[4-hydroxy-4-phenyl-(1*E*)-butenyl]-(4*Z*)-(1-trimethylsilylethylidene)-chroman (**2k**): IR (neat) 3381 (m), 3030 (m), 2953 (s), 1589 (s), 1481 (s), 1304 (s), 1250 (s), 1038 (s), 837 (s), 754 (s), 700 (s), cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.11 (s, 9 H), 1.84 (s, 3 H), 2.34 (m, 1 H), 3.57 (m, 1 H), 4.20 (d, *J* = 3.1, 10.8 Hz, 1 H), 4.36 (d, *J* = 2.0, 10.8 Hz, 1 H), 4.45 (ddd, *J* = 3.1, 4.8, 7.9 Hz, 1 H), 5.40 (ddt, *J* = 1.5, 15.8, 7.8 Hz, 1 H), 5.57 (dd, *J* = 5.5, 15.8 Hz, 1 H), 6.75 (dd, *J* = 1.1, 7.7 Hz, 2 H), 6.81 (dd, *J* = 1.1, 7.7 Hz, 2 H), 7.31 – 7.41 (m, 7 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 0.7, 18.7, 39.7, 42,8, 71.3, 73.2, 115.6, 119.3, 123.7, 125.8, 127.3, 128.0, 128.3, 128.5, 129.5, 130.5, 132.3, 143.7, 153.9; HRMS calcd for $C_{24}H_{30}O_2Si$: 378.2015. Found *m/z* (relative intensity): 379 (M^++1, 39), 378.2017 (M^+, 100), 107 (50), 73 (58).

(3S*,4'S*)-3-[4-hydroxy-4-phenyl-(1*E*)-butenyl]-(4*Z*)-(1-phenylethylidene)chromane (**2l**): IR (neat) 3391 (s), 2872 (s), 1738 (w), 1601 (m), 1574 (m), 912 (w), 824 (w), 748 (m) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.13 (s, 3 H), 2.34 – 2.44 (m, 2 H), 3.57 (m, 1 H), 4.32 (dd, *J* = 2.8, 11.0 Hz, 1 H), 4.42 (dd, *J* = 2.2, 11.0 Hz, 1 H), 4.49 (m, 1 H), 5.50 (ddt, *J* = 1.5, 15.4, 7.7 Hz, 1 H), 5.66 (dd, *J* = 5.3, 15.4 Hz, 1 H), 6.40 (ddd, *J* = 1.3, 7.0, 8.3 Hz, 1 H), 6.52 (dd, *J* = 1.5, 8.3 Hz, 1 H), 6.74 (dd, *J* = 1.3, 8.4 Hz, 1 H), 7.18 – 7.40 (m, 10 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.1, 22.3, 22.7, 38.1, 39.7, 42.5, 42.8, 70.4, 71.5, 73.3, 116.3, 119.4, 121.1, 125.6, 125.9, 126.0, 126.8, 128.3, 128.6, 129.1, 130.9, 131.2, 131.9, 132.1, 143.7, 144.4, 154.0; HRMS calcd for $C_{27}H_{26}O_2$: 382.1933. Found *m/z* (relative intensity): 383 (M^++1, 34),

382.1917 (M^+, 100), 275 (33), 107 (47).

(4S*,4'R*)-3-Iospropylidene-4-[4-hydroxy-6-phenyl-(1*E*)-hexenyl]-*N*-(*p*-toluene-sulfonyl)pyrrolidine (**2ca**): IR (neat) 3449 (s), 1340 (s), 1157 (s), 1092 (s), 1016 (s), 972 (m) cm^{-1}; ^1H NMR (400 MHz, C_6D_6) δ 1.21 (s, 3 H), 1.35 (s, 3 H), 1.58 (dm, *J* = 12.8 Hz, 1 H), 1.63 (dm, *J* = 12.8 Hz, 1 H), 1.87 (m, 1 H, coalescing to br dd, *J* = 6.6, 13.6 Hz, by irradiation at 5.22), 1.89 (s, 3 H), 1.94 (m, 1 H, coalescing to br dd, *J* = 4.4, 13.6 Hz, irradiation at 5.22), 2.60 (br dt, *J* = 13.6, 8.1 Hz, 1 H), 2.73 (br ddd, *J* = 6.6, 8.1, 13.6 Hz, 1 H), 2.89 (br dt, *J* = 2.2, 6.6 Hz, 1 H), 2.99 (br dd, *J* = 6.6, 9.2, 1 H), 3.34 (dd, *J* = 2.2, 9.2 Hz, 1 H), 3.36 (ddm, *J* = 4.4, 6.6 Hz, 1 H), 3.60 (br d, *J* = 13.6 Hz, 1 H), 4.00 (br d, *J* = 13.6 Hz, 1 H), 5.22 (ddd, *J* = 6.6, 9.2, 15.4 Hz, 1 H), 5.28 (ddd, *J* = 6.6, 15.4, 1 H), 6.80 (d, *J* = 8.1 Hz, 2 H), 7.07 – 7.22 (m, 5 H), 7.76 (d, *J* = 8.1 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.5, 21.3, 21.6, 32.1, 38.5, 40.6, 44.3, 50, 54.3, 70.3, 125.9, 126.3, 126.5, 128.0, 128.5, 129.7, 130.1, 132.6, 133.6, 134.6, 142.1, 143.6; HRMS calcd for $C_{26}H_{33}O_3NS$: 439.2181. Found *m/z* (relative intensity): 439.2114 (M^+, 3), 438 (2), 305 (100), 238 (33), 105 (16).

(4S*,4'S*)-3-Isopropylidene-4-[4-cyclohexyl-4-hydroxy-(1*E*)-butenyl]-*N*-(*p*-toluenesulfonyl)pyrrolidene (**2cb**): IR (neat) 3447 (s), 1340 (s), 1159 (s), 970 (s), 710 (s) cm^{-1}; ^1H NMR (400 MHz, C_6D_6) δ 0.96 – 1.29 (m, 6 H), 1.21 (s, 3 H), 1.38 (s, 3 H), 1.54 – 1.88 (m, 5 H), 1.90 (s, 3 H), 1.94 (ddm, *J* = 7.3, 9.2, 13.2 Hz, 1 H), 2.05 (ddm, *J* = 3.1, 6.2, 13.2 Hz, 1 H), 2.94 (br ddd, *J* = 2.0, 6.6, 7.3 Hz, 1 H), 3.02 (dd, *J* = 6.6, 9.2 Hz, 1 H), 3.18 (ddd, *J* = 3.1, 5.3, 9.2 Hz, 1 H), 3.35 (dd, *J* = 2.0, 9.2 Hz, 1 H), 3.61 (br d, *J* = 13.6 Hz, 1 H), 4.00 (br d, *J* = 13.6 Hz, 1 H), 5.27 (dd, *J* = 7.3, 15.0 Hz, 1 H), 5.37 (ddd, *J* = 6.2, 7.3, 15.0 Hz, 1 H), 6.81 (d, *J* = 8.2 Hz, 2 H), 7.77 (d, *J* = 8.2 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.5, 21.3, 21.6, 26.2, 26.4, 26.6, 28.2, 29.2, 37.4, 43.2, 44.3, 50.5, 54.3, 75.1, 126.4, 127.1, 128.0, 129.7, 130.2, 132.6, 133.2, 143.6; HRMS calcd for $C_{24}H_{35}O_3NS$: 417.2338. Found *m/z* (relative

intensity): 417.2376 (M^+, 4), 416 (4), 305 (100), 262 (40), 107 (21).

(4S*,4'S*)-3-Isopropylidene-4-[4-*tert*-butyl-4-hydroxy-(1*E*)-butenyl]-*N*-(*p*-toluenesulfonyl)pyrrolidine (**2cc**): a mixture of two diastereomers in a ratio of 12:1; IR (neat) 3553 (s), 1346 (s), 1159 (s), 1094 (s), 970 (s), 710 (s) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, major isomer) δ 0.90 (s, 9 H), 1.55 (br s, 3 H), 1.58 (br s, 3 H), 1.88 (ddd, *J* = 7.3, 10.6, 13.9 Hz, 1 H), 2.27 (ddd, *J* = 2.2, 5.3, 13.9 Hz, 1 H), 2.43 (s, 3 H), 3.11 (dd, *J* = 6.4, 9.2 Hz, 1 H), 3.18 (dd, *J* = 2.2, 10.6 Hz, 1 H), 3.29 (br t, *J* = 6.4 Hz, 1 H), 3.33 (dd, *J* = 2.2, 9.2 Hz, 1 H), 3.57 (br d, *J* = 13.6 Hz, 1 H), 3.90 (br d, *J* = 13.6 Hz, 1 H), 5.42 (dd, *J* = 6.4, 15.2 Hz, 1 H), 5.46 (ddd, *J* = 5.3, 7.3, 15.2 Hz, 1 H), 7.33 (d, *J* = 8.4 Hz, 2 H), 7.71 (d, *J* = 8.4 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$, major isomer) δ 20.5, 21.3, 21.6, 25.8, 34.7, 35.1, 44.3, 50.4, 54.3, 78.5, 126.5, 128.0, 128.1, 129.7, 130.3, 132.6, 133.2, 143.6; HRMS calcd for $C_{22}H_{33}O_3NS$: 391.2181.Found *m*/*z* (relative intensity): 391.2134 (M^+, 3), 374 (100), 236 (56), 108 (23).

3-Isopropylidene-4-[hydroxy-4,4-pentamethyl-(1*E*)-butenyl]-*N*-(*p*-toluenesulfonyl)pyrrolidine (**2cd**): IR (neat) 3553 (s), 1242 (m), 1015 (m), 972 (m), 710 (m) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.34 – 1.58 (m, 10 H), 1.56 (br s, 3 H), 1.57 (br s, 3 H), 1.57 (br s, 3 H), 2.10 (d, *J* = 7.3 Hz, 2 H), 2.43 (s, 3 H), 3.13 (dd, *J* = 7.3, 9.5 Hz, 1 H), 3.30 (dd, *J* = 2.6, 9.5 Hz, 1 H), 3.30 (m, 1 H), 3.58 (br d, *J* = 13.4 Hz, 1 H), 3.89 (br d, *J* = 13.4 Hz, 1 H), 5.35 (dd, *J* = 7.3, 15.0 Hz, 1 H), 5.47 (dt, *J* = 15.0, 7.3 Hz, 1 H), 7.33 (d, *J* = 8.2 Hz, 2 H), 7.71 (d, *J* = 8.2 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.5, 21.3, 21.5, 22.2, 25.8, 37.5, 44.3, 45.2, 50.4, 54.4, 71.1, 125.5, 126.3, 128.0, 129.6, 130.3, 133.0, 133.8, 143.5; HRMS calcd for $C_{23}H_{33}O_3NS$: 403.2181. Found *m*/*z* (relative intensity): 403.2174 (M^+, 1), 305 (100), 262 (36), 99 (25), 91 (39).

(2*E*)-(1-Phenylethylidene)-3-[4-hydroxy-4,4-pentamethylene-(1*E*)-butenyl]-5,5-

diphenylcyclopentaol (**2fd**): major isomer: mp 43.0 – 44.0 ℃ (hexane – dichloromethane); IR (KBr disk) 3422 (w), 3057 (w), 2932 (s), 1599 (w), 1493 (m), 1447 (m), 1005 (m), 970 (m), 700 (s) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.39 – 1.64 (m, 10 H), 1.95 (br s, 3 H), 2.21 (d, *J* = 7.0 Hz, 2 H), 2.69 (dd, *J* = 8.1, 12.3 Hz, 1 H), 2.79 (dd, *J* = 9.7, 12.3 Hz, 1 H), 3.18 (dt, *J* = 9.7, 8.1 Hz, 1 H), 4.78 (s, 1 H), 5.58 (dt, *J* = 15.0, 7.0 Hz, 1 H), 5.68 (dd, *J* = 8.1, 15.0 Hz, 1 H), 7.01 – 7.44 (m, 15 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.4, 22.3, 25.8, 29.7, 37.5, 42.0, 43.3, 45.3, 59.0, 71.2, 78.8, 124.9, 125.9, 126.4, 127.0, 127.0, 127.2, 127.9, 128.0, 128.1, 128.2, 128.7, 137.3, 138.1, 140.5, 143.8, 144.4, 145.8; HRMS calcd for $C_{34}H_{38}O_2$–H_2O: 460.2766. Found *m*/*z* (relative intensity): 460.2792 (M^+-H_2O, 100), 99 (32). minor isomer: ^1H NMR (400 MHz, $CDCl_3$) δ 1.10 – 1.72 (m, 10 H), 1.92 (ddd, *J* = 1.1, 7.3, 12.5 Hz, 1 H), 1.98 (br s, 3 H), 2.30 (ddd, *J* = 1.1, 2.6, 12.5 Hz, 1 H), 3.29 (dd, *J* = 9.5, 12.5 Hz, 1 H), 3.68 (br dd, *J* = 8.4, 9.5 Hz, 1 H), 4.82 (dd, *J* = 8.4, 15.4 Hz, 1 H), 5.02 (s, 1 H), 5.43 (br ddt, *J* = 15.4, 7.3 Hz, 1 H), 7.13 – 7.39 (m, 15 H).

(2*E*)-(1-Phenylethylidene)-3-[4-hydroxy-4,4-dimethyl-(1*E*)-butenyl]-5,5-diphenylcyclopentanol (**2fe**): a mixture of two diastereomers in a ratio of 3:1; mp 64.0 – 65.0 ℃ (hexane – dichloromethane); IR (KBr disk) 3395 (m), 3055 (w), 2968 (m), 1599 (w), 1493 (m), 1375 (m), 1055 (m), 700 (s) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.21 (s, 6 H, major isomer), 1.25 (s, 6 H, minor isomer), 1.95 (d, *J* = 1.1 Hz, 3 H, major isomer), 2.17 (br s, 3 H, minor isomer), 2.23 (d, *J* = 7.3 Hz, 2 H), 2.70 (ddm, *J* = 8.1, 2.3 Hz, 1 H), 2.80 (dd, *J* = 9.7, 12.3 Hz, 1 H), 3.18 (dt, *J* = 9.7, 8.1 Hz, 1 H), 4.78 (s, 1 H), 5.58 (dt, *J* = 15.0, 7.3 Hz, 1 H), 5.69 (dd, *J* = 8.1, 15.0 Hz, 1 H), 7.01 – 7.44 (m, 15 H); ^{13}C NMR (100 MHz, $CDCl_3$, a major isomer is assigned) δ 20.3, 29.1, 41.9, 43.2, 46.8, 59.0, 70.6, 78.8, 125.4, 125.9, 126.4, 127.0, 127.2, 127.8, 128.0, 128.2, 128.7, 137.4, 138.1, 140.4, 143.7, 144.3, 145.8; HRMS calcd for $C_{31}H_{34}O_2$–H_2O: 420.2453. Found *m*/*z* (relative intensity): 420.2445 (M^+-H_2O, 100).

(1S*,4'R*)-2-Isopropylidene-1-[4-hydroxy-6-phenyl-(1*E*)-hexenyl]-5,5-dicarbomethoxycyclohexane (**2ma**): a mixture of two diastereomers in a ratio of 8:1; IR (neat) 3466 (m), 2928 (m), 1732 (s), 1435 (m), 1242 (s), 1200 (m), 1051 (w), 700 (m) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, a major isomer assigned) δ 1.60 (br s, 3 H), 1.70 (br s, 3 H), 1.72 – 1.78 (m, 2 H), 2.02 (dm, *J* = 13.9 Hz, 1 H), 2.04 (ddm, *J* = 8.8, 13.9 Hz, 1 H), 2.17 (dm, *J* = 13.9 Hz, 2 H), 2.25 (m, 1 H), 2.36 (m, 1 H), 2.40 (dt, *J* = 13.9 Hz, 1 H), 2.49 (br d, *J* = 13.9 Hz, 1 H), 2.68 (ddm, *J* = 9.2, 13.7 Hz, 1 H), 2.80 (ddd, *J* = 5.9, 9.2, 13.7 Hz, 1 H), 3.47 (br s, 1 H), 3.59 (m, 1 H), 3.68 (s, 3 H), 3.72 (s, 3 H), 5.17 (dddm, *J* = 5.9, 8.8, 15.4 Hz, 1 H), 5.41 (br dd, *J* = 4.2, 15.4 Hz, 1 H), 7.15 – 7.32 (m, 5 H); ^{13}C NMR (100 MHz, $CDCl_3$, a major isomer is assigned) δ 19.9, 20.1, 22.4, 31.4, 32.1, 35.8, 38.4, 41.3, 52.5, 70.2, 125.4, 125.8, 126.3, 128.4, 128.5, 135.2, 135.2, 142.4, 172.8; HRMS calcd for $C_{25}H_{34}O_5$; 414.2406. Found *m*/*z* (relative intensity): 414.2408 (M^+, 84), 396 (M^+-H_2O), 242 (100), 105 (33).

(1S*,4'S*)-2-Isopropylidene-1-[4-hydroxy-4-cyclohexyl-(1*E*)-hexenyl]-5,5-dicarbomethoxycyclohexane (**2mb**): IR (neat) 3555 (m), 2926 (s), 1732 (s), 1450 (s), 1242 (s), 1200 (s), 1087 (m), 978 (m), 756 (w) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.99 – 1.33 (m, 6 H), 1.55 – 1.76 (m, 5 H), 1.61 (br s, 3 H), 1.70 (s, 3 H), 1.85 (d, *J* = 3.1 Hz, 1 H), 1.96 (dd, *J* = 9.2, 13.9 Hz, 1 H), 1.99 (dd., *J* = 9.2, 13.9 Hz, 1 H), 2.17 (dd, *J* = 5.9, 13.9 Hz, 1 H), 2.20 – 2.29 (m, 2 H), 2.36 (m, 1 H), 2.40 (dm, *J* = 13.9 Hz, 1 H), 2.50 (br dt, *J* = 14.7, 3.7 Hz, 1 H), 3.31 (ddm, *J* = 5.5, 11.7 Hz, 1 H), 3.48 (m, 1 H), 3.68 (s, 3 H), 3.73 (s, 3 H), 5.19 (dddm, *J* = 5.5, 9.2, 15.4 Hz, 1 H), 5.40 (dm, *J* = 15.4 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.9, 20.1, 22.4, 26.3, 26.4, 26.6, 28.4, 29.1, 31.4, 35.9, 37.9, 38.5, 43.4, 52.5, 75.0, 125.3, 127.0, 128.7, 134.9, 172.7, 172.7, 172.8; HRMS calcd for $C_{23}H_{36}O_5$: 392.2563. Found *m*/*z* (relative intensity): 392.2539 (M^+, 60), 265 (71), 239 (10), 113 (39).

(1S*,4'S*)-2-Isopropylidene-1-[4-hydroxy-4-*tert*-butyl-(1*E*)-hexenyl]-5,5-

dicarbomethoxycyclohexane (**2mc**): IR (neat) 3553 (s), 2959 (s), 1724 (s), 1437 (s), 1290 (s), 1252 (s), 1202 (s), 1088 (s), 980 (s), 698 (w) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.90 (s, 9 H), 1.61 (br s, 3 H), 1.70 (s, 3 H), 1.84 (br d, *J* = 2.7 Hz, 1 H), 1.85 (ddm, *J* = 9.7, 13.7 Hz, 1 H), 1.87 (ddm, *J* = 10.3, 13.7 Hz, 1 H), 2.17 (dm, *J* = 13.9 Hz, 1 H), 2.23 – 2.30 (m, 2 H), 2.36 (dm, *J* = 14.3 Hz, 1 H), 2.41 (dm, *J* = 13.9 Hz, 1 H), 2.50 (dm, *J* = 14.3 Hz, 1 H), 3.19 (ddm, *J* = 2.7, 10.3 Hz, 1 H), 3.49 (m, 1 H), 3.68 (s, 3 H), 3.73 (s, 3 H), 5.19 (ddm, *J* = 9.7, 15.4 Hz, 1 H), 5.41 (dm, *J* = 15.4 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.9, 20.1, 22.3, 25.9, 31.4, 34.6, 35.8, 35.9, 38.4, 52.5, 78.3, 125.3, 127.8, 128.7, 134.9, 172.7, 172.8; HRMS calcd for $C_{21}H_{34}O_5$: 366.2406. Found *m*/*z* (relative intensity): 366.2424 (M^+, 38), 309 (17), 280 (100), 265 (16), 127 (13), 91 (14).

2-[4-hydroxy-4-pentamethylene-(1*E*)-butenyl]-4,4-dicarbomethoxyisopropylidenecyclohexane (**2md**): IR (neat) 3474 (m), 2932 (s), 1734 (s), 1437 (s), 1242 (s), 1088 (m), 978 (m), 733 (w) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.19 – 1.67 (m, 11 H), 1.61 (br s, 3 H), 1.70 (s, 3 H), 2.09 (d, *J* = 7.3 Hz, 2 H), 2.16 (dm, *J* = 13.2 Hz, 1 H), 2.18 (d, *J* = 13.2 Hz, 1 H), 2.25 (dm, *J* = 13.9 Hz, 1 H), 2.36 (dm, *J* = 14.7 Hz, 1 H), 2.41 (dm, *J* = 13.9 Hz, 1 H), 2.50 (dm, *J* = 14.7 Hz, 1 H), 3.49 (m, 1 H), 3.68 (s, 3 H), 3.72 (s, 3 H), 5.29 (dtm, *J* = 7.3, 15.4 Hz, 1 H), 5.40 (dm, *J* = 15.4 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.9, 20.1, 22.3, 22.4, 26.0, 31.4, 36.0, 37.4, 37.8, 38.7, 45.4, 52.6, 71.1, 124.6, 125.1, 128.8, 135.8, 172.5, 172.8; HRMS calcd for $C_{22}H_{34}O_5$: 378.2406. Found *m*/*z* (relative intensity): 378.2389 (M^+, 30), 361 (21), 265 (32), 239 (94), 99 (100).

4,4-diethoxycarbonyl-2-[4-hydroxy-4-phenyl-(1*E*)-butenyl]-(1*Z*)-2-butylidenecyclopentane (**2m**): IR (neat) 3466 (s), 1732 (s), 1258 (s), 1194 (s), 1063 (s), 970 (m), 700 (s) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.91 (t, *J* = 7.7 Hz, 3 H), 1.23 (t, *J* = 7.3 Hz, 3 H), 1.25 (t, *J* = 7.3 Hz, 3 H), 1.64 (br s, 3 H), 1.96 (qm, *J* = 7.7 Hz, 2 H), 2.10 (dd, *J* = 4.8,

13.0 Hz, 1 H), 2.32 (d, *J* = 2.9 Hz, 1 H), 2.39 (ddd, *J* = 6.2, 7.7, 13.9 Hz, 1 H), 2.43 (dddm, *J* = 6.2, 7.7, 13.9 Hz, 1 H), 2.55 (dd, *J* = 8.4, 13.0 Hz, 1 H), 2.81 (d, *J* = 16.7 Hz, 1 H), 2.98 (d, *J* = 16.7 Hz, 1 H), 3.35 (dddm, *J* = 4.8, 6.2, 8.4 Hz, 1 H), 4.17 (q, *J* = 7.3 Hz, 2 H), 4.18 (q, *J* = 7.3 Hz, 2 H), 4.67 (ddd, *J* = 2.9, 6.2, 7.7 Hz, 1 H), 5.33 (br ddd, *J* = 6.2, 7.7, 15.4 Hz, 1 H), 5.45 (dd, *J* = 6.2, 15.4 Hz, 1 H), 7.22 – 7.36 (m, 5 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 12.5, 14.1, 18.3, 27.5, 38.8, 40.8, 43.0, 43.8, 59.2, 61.5, 61.6, 73.6, 125.4, 125.8, 127.3, 128.4, 131.7, 144.1, 172.0, 172.4. Anal. Calcd for $C_{25}H_{34}O_5$: C, 72.43; H, 8.27. Found: C, 72.18; H, 8.28.

3-[(1*E*)-a-Phenethylidene]-4-[4-hydroxy-4-phenyl-(1*E*)-butenyl]tetrahydrofuran (2n): a mixture of two diastereomers in a ratio of 8:1; IR (neat) 3418 (s), 1599 (m), 1028 (m), 968 (m), 700 (s) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, major isomer) δ 1.94 (s, 3 H), 2.15 (dt, *J* = 13.9, 8.4 Hz, 1 H), 2.25 (dddm, *J* = 4.4, 6.2, 13.9 Hz, 2 H), 3.45 (m, 1 H), 3.65 (dd, *J* = 3.9, 8.4 Hz, 1 H), 3.91 (dd, *J* = 6.2, 8.4 Hz, 1 H), 4.35 (dd, *J* = 4.4, 8.4 Hz, 1 H), 4.44 (br d, *J* = 13.6 Hz, 1 H), 4.48 (d, *J* = 13.6 Hz, 1 H), 4.99 (ddd, *J* = 6.2. 8.4, 15.0 Hz, 1 H), 5.30 (dd, *J* = 8.4, 15.0 Hz, 1 H), 7.17-7.35 (m, 10 H); ^{13}C NMR (100 MHz, $CDCl_3$, major isomer) δ 21.6, 42.9, 45.9, 70.8, 73.1, 74.8, 125.8, 126.5, 127.4, 127.7, 128.2, 128.3, 128.7, 134.0, 137.6, 143.2, 143.9; HRMS calcd for $C_{22}H_{24}NO_2S$: 320.1776, Found *m/z* (relative intensity): 320.1792 (M^+, 23), 302 (15), 214 (52), 183 (100), 108 (86).

2-Isopropylidene-4-oxa-1,6,6-triphenylundeca-8,10-dien-1-ol (**3**): IR (neat) 3477 (m), 3026 (m), 2916 (m), 1653 (w), 1601 (w), 1495 (m), 1447 (m), 1092 (s), 1009 (s), 901 (s), 756 (s), 700 (s) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.75 (s, 3 H), 1.89 (s, 3 H), 2.84 (dd, *J* = 7.3, 13.7 Hz, 1 H), 2.94 (d, *J* = 8.3 Hz, 1 H), 3.00 (dd, *J* = 7.3, 13.7 Hz, 1 H), 3.59 (d, *J* = 10.6 Hz, 1 H), 3.72 (d, *J* = 8.5 Hz, 1 H), 3.85 (d, *J* = 8.5 Hz, 1 H), 4.10 (d, *J* = 10.6 Hz, 1 H), 4.92 (d, *J* = 10.5 Hz, 1 H), 5.02 (d, *J* = 16.8 Hz, 1 H), 5.20 (dt, *J* = 15.0, 7.3 Hz, 1 H), 5.60 (d, *J* = 8.3 Hz,

1 H), 5.95 (dd, *J* = 10.5, 15.0 Hz, 1 H), 6.15 (dt, *J* = 16.8, 10.5 Hz, 1 H), 7.00 (d, *J* = 7.1 Hz, 2 H), 7.06 (d, *J* = 7.1 Hz, 2 H), 7.13 – 7.33 (m, 11 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.8, 39.8, 50.3, 68.5, 72.2, 75.8, 115.2, 125.3, 126.1, 126.2, 127.5, 127.7, 127.8, 127.9, 128.0, 130.2, 130.4, 133.7, 134.0, 136.9, 143.8, 145.6, 145.8; HRMS calcd for $C_{31}H_{34}O_2$: 438.2559. Found *m/z* (relative intensity): 439 (M^++1, 29), 438.2581 (M^+, 100),421 (M^+, 35).

(4*E*)-7,7-Diethoxycarbonyl-1-phenyl-4-undecene-9-yn-1-ol (**4**): IR (neat) 3443 (s), 1732 (s), 1192 (s), 1028 (s), 972 (m), 702 (s) cm^{-1}; ^{1}H NMR (400 MHz, C_6D_6) δ 0.91 (t, *J* = 7.0 Hz, 3 H), 0.92 (t, *J* = 7.0 Hz, 3 H), 1.46 (t, *J* = 2.6 Hz, 3 H), 1.62 (ddt, *J* = 5.1, 15.2, 7.3 Hz, 1 H), 1.75 (dq, *J* = 15.2, 7.3 Hz, 1 H), 2.04 (q, *J* = 7.3 Hz, 2 H), 3.15 (q, *J* = 2.6 Hz, 2 H), 3,17 (d, *J* = 6.8 Hz, 2 H), 3.99 (q, *J* = 7.0 Hz, 4 H), 4.41 (dd, *J* = 5.1, 7.3 Hz, 1 H), 5.51 (br dt, *J* = 15.0, 7.3 Hz, 1 H), 5.63 (br dt, *J* = 15.0, 6.8 Hz, 1 H), 7.05 – 7.30 (m, 5 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 3.4, 14.1, 22.9, 28.9, 35.2, 38.5, 57.3, 61.4, 61.5, 73.5, 73.8, 78.6, 124.1, 125.9, 127.5, 128.5, 134.7, 144.7, 170.2. Anal. Calcd for $C_{23}H_{30}O_5$: C, 71.48; H, 7.82. Found: C, 71.27; H, 7.70.

Reference

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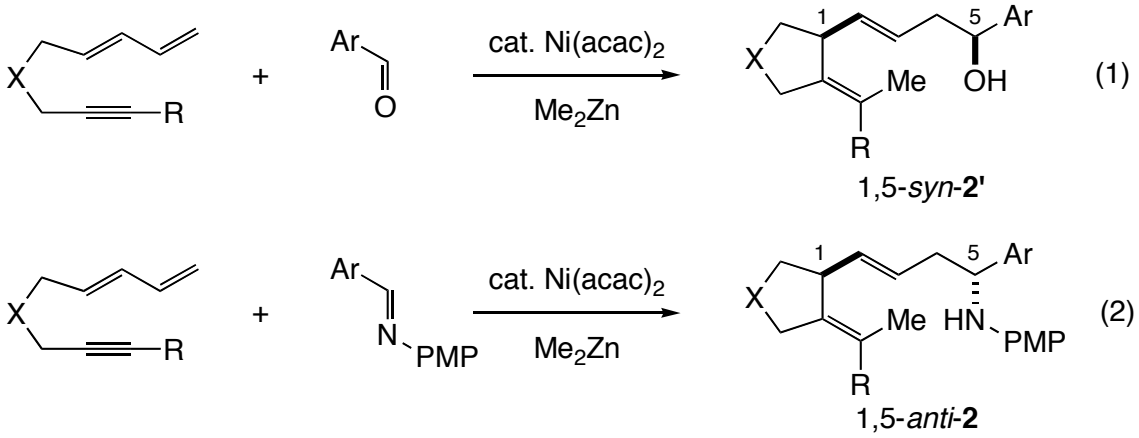
第４章

ニッケル触媒を用いるジメチル亜鉛、１，ω－ジエンイン、アルデヒド、アミンの多成分連結反応の開発

４－１　緒言

アルドイミンは反応性が低い親電子剤の１つである。典型有機金属を用いるアルドイミンの炭素－炭素結合形成反応は、アルデヒドやアミン部位に電子吸引基を導入し、アルドイミンを活性化する必要があるため、必ずしも実用的であるとは言えない。[1],[2] 遷移金属触媒を用いる反応では、アルデヒドとアルドイミンの間にそれほど大きな反応性の違いはなく、実際に、アルドイミンがアルデヒドに匹敵する反応性を示す例が報告されている。[3],[4]　前章で述べたように、ニッケル触媒存在下、ジメチル亜鉛、１，ω－ジエンイン、アルデヒドを反応させると、四成分連結反応が環化を伴い、室温で速やかに進行し、ホモアリルアルコール **2'**を高収率で与え、高い１，５－*syn* ジアステレオ選択性を示す（式１）。[5]　アルドイミンの場合も同様の反応性を示すが、立体選択性が逆転し、１，５－*anti* ジアステレオ選択的にホモアリルアミン **2** を与えることを発見した（式２）。[6]



Scheme 1. Completely Opposite 1,5-Diastereoselectivity between Aldehydes and Aldimines.

アルドイミンの反応では、１，５位の相対立体配置がアルデヒドの反応とは全く逆になる点が非常に興味深い。アルデヒドの反応では、１，５－ジアステレオ選択性が*anti*／*syn*＝１：７～１：＞３０であるのに対して、アルドイミンの反応では、１，５－*anti* 体を単一のジアステレオマーで与える。単離収率もアルドイミンの反応の方が高い。さらに、アルデヒドとアミンの脱水縮合により生成するアルドイミンを別途単離する必要がなく、すなわち、脱水で生じる水を取り除くことなく反応に用いることができる。実質的には五成分を一挙に連結し、かつ環化生成物を高選択的に与える点で合成的意義が高い。さらに、本反応は、ラクトールとアミンから生成する *N, O*－アセタールにも適用が可能であり、１，５－*anti* ジアステレオ選択的に環状のジエニルアミノアルコールを与えることも発見した。

本章では、種々の有機亜鉛、１，ω－ジエンイン、アルデヒドまたはラクトール、アミンを用いた多成分連結反応の反応性、選択性について報告する。

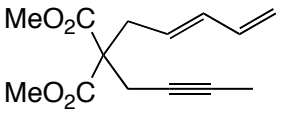
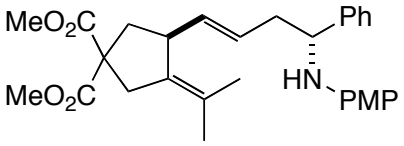
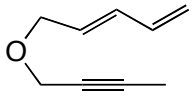
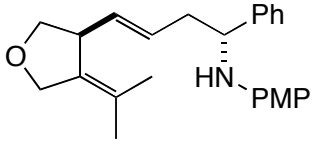
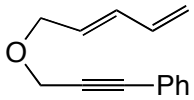
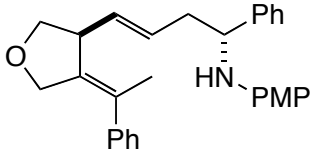
４－２　結果及び考察

４－２－１　ニッケル触媒を用いるジメチル亜鉛、１，ω－ジエンイン、アルドイミンの多成分連結反応

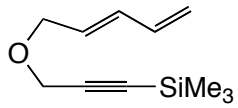
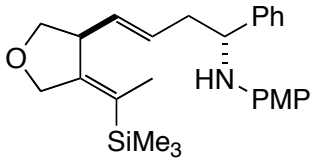
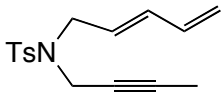
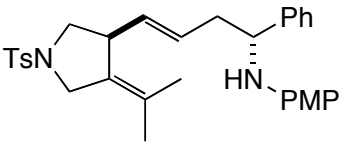
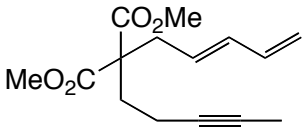
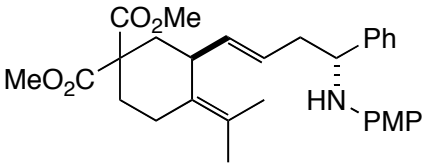
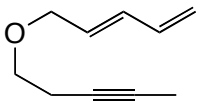
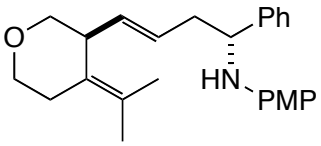
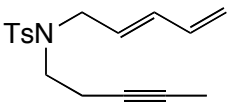
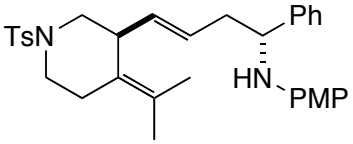
１，ω－ジエンインの検討を行った。常圧窒素雰囲気下、ベンズアルデヒド（1 mmol）と *p*－アニシジン（2 mmol）を THF（2 ml）中、室温で 12 時間反応させ、アルドイミンを生成した。それに、THF（1 ml）に溶解させたニッケルアセチルアセトナト（0.05 mmol）を cannula 法によって添加し、１，ω－ジエンイン（0.5 mmol）、ジメチル亜鉛 1M ヘキサン溶液（3.6 ml）を順に加えて反応を行った。

その結果を Table 1 に示す。

Table 1. Nickel-Catalyzed Coupling of Me_2Zn and Benzaldehyde-*p*-Anisidine Imine Across 1,ω-Dienynes **1**[a]

Run	1,ω-Dienyne **1**	Time (h)	% Isolated yield of product **2**
1	 **1a**	1	 **2a**: 95
2	 **1b**	1	 **2b**: 79
3	 **1c**	24[b]	 **2c**: 62

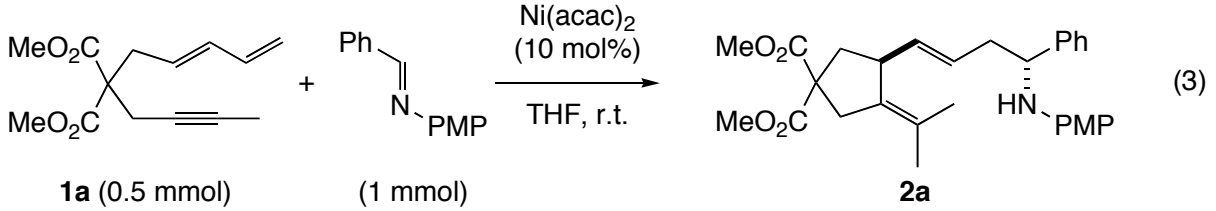
(Table 1 continued.)

4	 **1d**	2		**2d**: 60
5	 **1e**	1		**2e**: 60
6	 **1f**	0.5		**2f**: 78
7	 **1g**	3		**2g**: 51
8	 **1h**	0.5		**2h**: 78

[a] Reaction conditions: Benzaldehyde (1 mmol) and *p*-methoxyaniline (2 mmol) in THF (1.5 ml) at room temperature over night, and then $Ni(acac)_2$ (0.05 mmol) dissolved in THF (1.5 ml), a 1,ω-Dienyne **1** (0.5 mmol), Me_2Zn (3.6 mmol in hexane) at room temperature under N_2 for the period of time indicated. PMP = *p*-methoxyphenyl. [b] At 50 ºC.

１，ω－ジエンイン **1a-1e** を用いた場合、速やかに反応が進行し、シクロペンタン誘導体 **2a**、テトラヒドロフラン誘導体 **2b-2d**、ピロリジン誘導体 **2e** を良好な収率、かつ単一のジアステレオマーで与えた（Runs 1-5）。アルキンにフェニル基が置換した **1c** は、加熱を要したが立体選択的に反応が進行した（Run 3）。アルキンの末端に立体的に嵩高いトリメチルシリル基を有する **1d** の場合も、室温で速やかに反応が進行した（Run 4）。**2c**、**2d** の NOE の測定結果より、ジメチル亜鉛のメチル基はジエン由来の置換基に対してアルキンにシス付加することが明らかになった（Figure 3）。本反応はアルキンの置換基の種類によらず進行するため、四置換アルケンを立体選択的に合成する方法としても有用である。**1f**、**1g**、**1h** を用いた場合も、高収率でシクロヘキサン誘導体 **2f**、テトラヒドロピラン誘導体 **2g**、ピペリジン誘導体 **2h** を与え、本反応が六員環形成に適用できることがわかった（Runs 6-8）。**2g** の立体構造は単結晶 X－線構造解析により決定した。その結果、環状のアリル位メチン炭素に結合した側鎖とその側鎖のアミノ基の１，５位の相対立体配置が *anti* 体であることが明らかになった。他の生成物に関しても同様の構造であると推定した（Figure 2）。

系中には、アルドイミンの生成で生じる水と過剰量のアミンが存在する。それらに反応を促進させる効果[7]があるのではないかと考え、単離したアルドイミンに、水、アミンを添加して反応を行った。その結果を Table 2 に示す。



(3)

1a (0.5 mmol)　　(1 mmol)　　**2a**

Table 2. Effect of Additives for the Reaction of 1,ω-Dienyne **1a** Isolated Aldimine (Benzaldehyde-*p*-Anisidine) and Me_2Zn.

Run	Additive (mmol)	Me_2Zn (mmol)	Time (h)	Yield of **2a** (%)
1	none	1.2[a]	19	0
2	H_2O (1)	2.4	1	19
3	*p*-Anisidine (1)	2.4	0.5	71
4	*p*-Anisidine (1), H_2O (1)	3.6[b]	0.5	85

[a] The amount of Me_2Zn used is the same as that optimized for the reactions with aldehydes (Scheme 1, eq 1). [b] The amount of Me_2Zn is the same as that applied to the reactions shown in Table 1.

単離したアルドイミンだけを用いて反応を行った場合、反応は完結せず、**2a** の生成は確認されなかった（Run 1）。水（1 mmol）、または、*p*－アニシジン（1 mmol）を添加した場合、速やかに反応が進行し、それぞれ **2a** を 19%、71%で与えた（Runs 2 and 3）。水と *p*－アニシジンが共存すると、さらに **2a** の収率が向上した（Run 4）。現在、水および *p*－アニシジンの役割は明確ではないが、*p*－アニシジンは、ジメチル亜鉛に配位してジメチル亜鉛の複雑なオリゴマーを簡単なオリゴマーもしくはモノマーに解離してジメチル亜鉛のイオン性を高めていることが考えられる。水は、ジメチル亜鉛と反応して何らかの亜鉛錯体を形成して、それがルイス酸として作用して、アルドイミンを活性化していることが予想される。

次にアルデヒドの検討を行った。反応系中で *p*－アニシジンと芳香族アルデヒド、あるいは脂肪族アルデヒドから生成したアルドイミンを Table 1 と同様の条件下で反応させた。その結果を Figure 1 に示す。

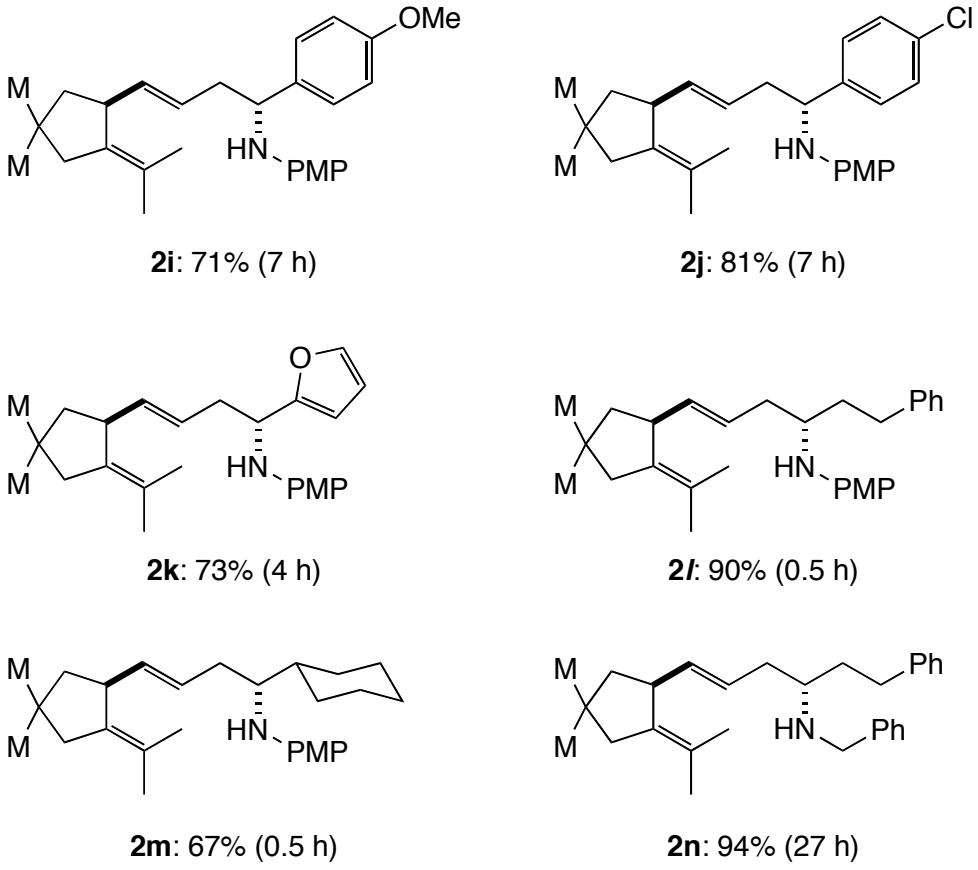


Figure 1. Nickel-Catalyzed Multi-Component Connection Reaction of Me_2Zn, 1,ω-Dienye **1a**, Aromatic and Aliphatic Aldehydes and Amines.

電子供与基や電子吸引基が置換した芳香族アルデヒドあるいはヘテロ芳香族アルデヒド、いずれも同様の反応性を示し、高収率で単一の環化生成物 **2i-2k** を与えた。興味深いことに、反応時間から判断して、脂肪族アルデヒドのイミンの方が芳香族アルデヒドのイミンよりも反応性が高いことが考えられる。さらに、ジヒドロシンナムアルデヒドとベンジルアミンから生成したアルドイミンも、同様の反応性を示し、定量的に **2n** を与えた。

次にフルフラールと各種アミンから生成したアルドイミンを用いて反応を行った。常圧窒素雰囲気下、フルフラール（1 mmol）と各種アミン（2 mmol）を THF（2 ml）中、室温で 12 時間反応させ、アルドイミンを生成した。それに、THF（1 ml）に溶解させたニッケルアセチルアセトナト（0.05 mmol）を cannula 法によって添加し、1，ω－ジエンイン **1a**（0.5 mmol）、ジメチル亜鉛 1M ヘキサン溶液（3.6 ml）を順に加えて反応を行った。その結果を Table 3 に示す。

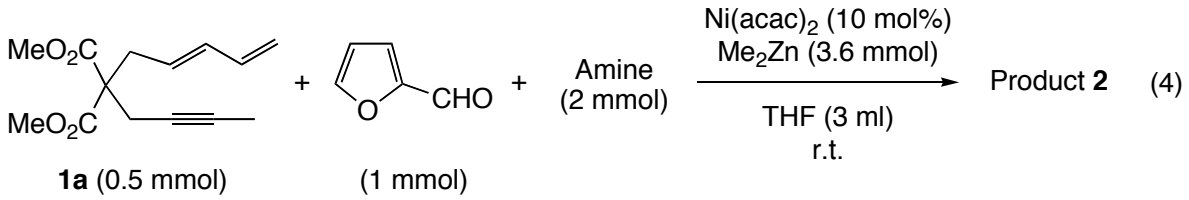
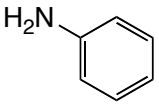
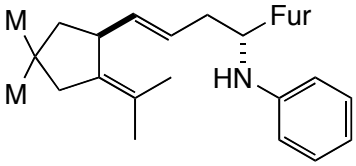
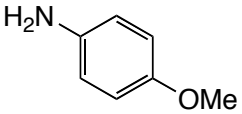
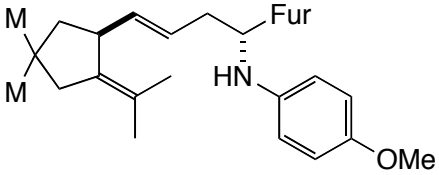
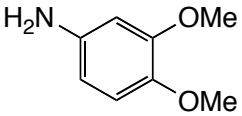
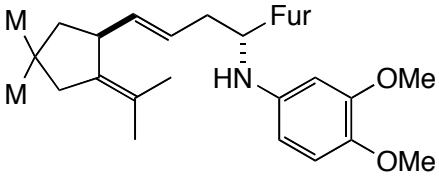
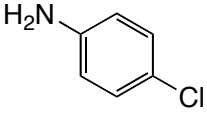
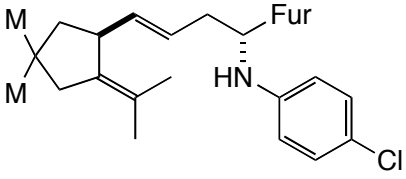
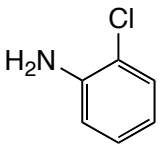
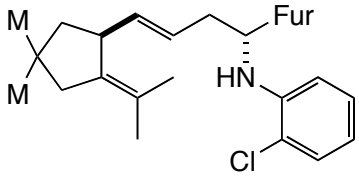
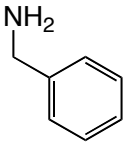
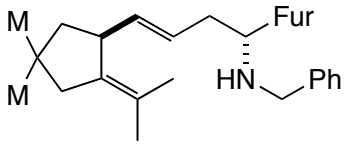


Table 3. Nickel-Catalyzed Conjugative Addition of Me_2Zn upon Aldimines Across 1,ω-Dienyne **1a**[a]

Run	Amine	Time (h)	% Isolated yield of product **2**
1[a]		1	 **2o**: 91
2[a]		6	 **2k**: 73
3[a]		0.5	 **2p**: 100
4[a]		2	 **2q**: 81

(Table 3 continued.)

5[b]		0.5		**2r**: 34
6[b]		5		**2s**: 74

[a] Reaction condition: Furfural (1 mmol) and an amine (2 mmol) in THF (1.5 ml) were reacted at room temperature for 12 h under N_2, and then $Ni(acac)_2$ dissolved in THF (1.5 ml), 1,ω-Dienyne **1a** (0.5 mmol), Me_2Zn (3.6 mmol, 1 M hexane) at room temperature under N_2 for the period of time indicated.
[b] Reaction condition: Furfual (1 mmol) and an amine (2 mmol) in THF (2 ml) were reacted at reflux for 0.5 h; distillation THF (azeotropic removal of water) under N_2, and then $Ni(acac)_2$ (0.05 mmol) was dissolved in THF (3 ml), 1,ω-Dienye **1a** (0.5 mmol), Me_2Zn (3.6 mmol, hexane) at room temperature under N_2 for period of time indicated.
M stands for CO_2Me.

芳香族アミンのパラ位に電子供与基、電子吸引基を導入したアルドイミンはジメチル亜鉛、１，ω－ジエンイン **1a** と室温で速やかに反応し、高収率で単一のホモアリルアミンを与えた（Runs 2 and 4）。オルト位が置換した芳香族アミンから生成したアルドイミンを用いると、著しく生成物の収率が低下した（Run 5）。メタ位とパラ位が電子供与基で置換した芳香族アミンから生成したアルドイミンを用いた場合には、速やかに反応が進行し、定量的に **2p** を与えた（Run 3）。ベンジルアミンとフルフラールから生成したアルドイミンを用いても、五成分連結反応が進行し、**2s** を良好な収率、かつ単一のジアステレオマーで与えた（Run 6）。

次に有機亜鉛の検討を行った。常圧窒素雰囲気下、ベンズアルデヒド（1 mmol）と *p*－アニシジン（2 mmol）を THF（2 ml）中、室温で 12 時間反応させ、アルドイミンを生成した。それに、THF (1 ml) に溶解させたニッケルアセチルアセトナト (0.05 mmol）を cannula 法によって添加し、１，ω－ジエンイン **1a**（0.5 mmol）、有機亜鉛（3.6 mmol）を順に加えて反応を行った。その結果を Table 4 に示す。

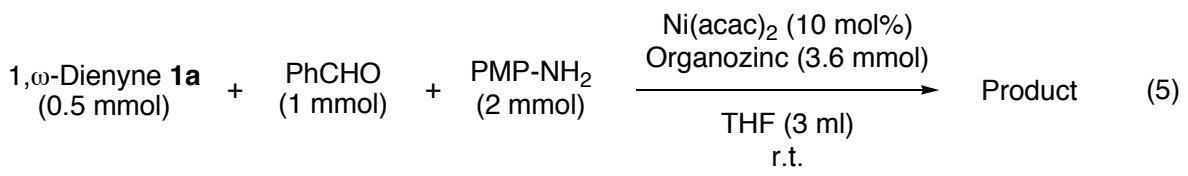
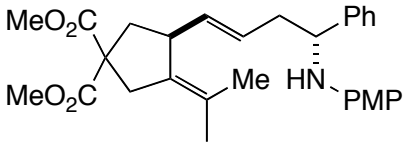
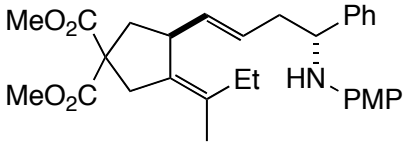
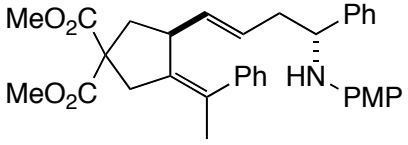
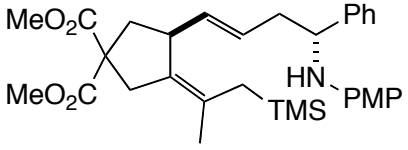


Table 4. Nickel-Catalyzed Coupling of Organozinc and Benzaldehyde-*p*-Anisidine Imine Across 1,ω-Dienynes **1**[a]

Run	Organozinc (mmol)	Time (h)	% Isolated yield of product
1	Me_2Zn (3.6)	1	 **2a**: 95
2	Et_2Zn (3.6)	0.5	 **3a**: 42
3	Ph_2Zn[b] (3.6)	0.5	Complex mixture
4	PhZnCl[c] (7.2)	2	 **4**: trace
5[d]	Ph_3B (3.6)	3	**4**: trace
6	$(TMSCH_2)_2Zn$[e] (3.6)	0.5	 **5**: 75

[a] Reaction condition: Benzaldehyde (1 mmol) and *p*-methoxyaniline (2 mmol) in THF (1.5 ml) were reacted at room temperature for 12 h under N_2, and then $Ni(acac)_2$ (0.05 mmol) was dissolved in THF (1.5 ml), 1,ω-Dienyne **1a** (0.5 mmol), Organozinc (3.6 mmol) at room temperature under N_2 for the period of time indicated.
[b] Ph_2Zn [prepared from PhMgBr (7.2 mmol, in THF) and $ZnCl_2$ (3.6 mmol in ether)].
[c] PhZnCl [prepared from PhMgBr (7.2 mmol, in THF) and $ZnCl_2$ (7.2 mmol in ether)].
[d] $Ni(cod)_2$ (0.05 mmol) was used as a catalyst.
[e] $(TMSCH_2)_2Zn$ [prepared from $TMSCH_2MgCl$ (7.2 mmol, in ether) and $ZnCl_2$ (3.6 mmol in ether)].
PMP and TMS stand for *p*-methoxyphenyl and trimethylsilyl group.

ジメチル亜鉛を用いた場合、五成分連結反応が室温で速やかに進行し、１，５位の相対立体配置が単一のホモアリルアミン **2a** を定量的に与えた（Run 1）。ジメチル亜鉛の代わりにβ－水素を有するジエチル亜鉛を用いた場合、反応は速やかに完結し、低収率ではあるがエチル基が導入した単一のホモアリルアミン **3a** を与えた（Run 2）。第三章で述べたように、アルデヒドとの反応では、ジエチル亜鉛、１，３－ジエン、アルデヒドのホモアリル化反応が選択的に進行し、ビスホモアリルアルコールを主生成物として与え、四成分連結反応によるホモアリルアルコールを副生成物として与える。すなわち、ジエチル亜鉛が還元剤およびエチル化剤として作用する。アルドイミンを用いた反応の場合、五成分連結反応が優先的に進行する理由として、反応系中に過剰に存在する水またはアミンがπ－アリルニッケル中間体 **II**（Scheme 4）の Ni(II) に配位して、Ni(II)とエチル基上のβ－水素とのアゴスティック相互作用を阻害するために、β－水素脱離が起こらず、π－アリルニッケルのアルキンへの付加が進行する。すなわち､ホモアリル化反応よりも五成分連結反応が選択的に進行すると考えられる。ジフェニル亜鉛を用いた場合には、反応が複雑となり、目的生成物の単離には至らなかった（Run 3）。PhZnCl やトリフェニルホウ素を用いると、若干量であるが、フェニル基が導入した環化生成物 **4** を与えた（Runs 4 and 5）。$(TMSCH_2)_2Zn$ を用いた場合には、ジメチル亜鉛と同様に速やかに反応が進行し、分子内にアリルシラン骨格を保持したホモアリルアミン **5** を良好な収率、かつ単一のジアステレオマーで与えた（Run 6）。

テトラヒドロピラン誘導体 **2g** は結晶性が良く、その立体構造は、単結晶 X－線構造解析により決定した（Figure 2）。[10] その結果、環状のアリル位メチン炭素に結合した側鎖と、その側鎖のアミノ基の１，５位の相対立体配置が *anti* 体であることが明らかになった。

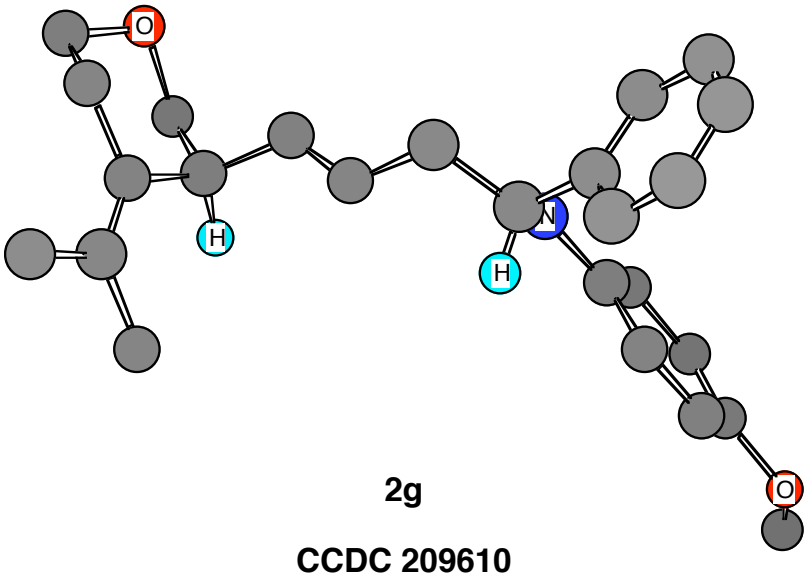


Figure 2. The Chem 3D^{TM} Presentation of X-Ray Structure of **2g**. For clarity, all protons except those on the stereogenic centers are omitted.

2c の環外二重結合の立体化学は NOE の測定により決定した（Figure 3）。メチル基への照射で、環のアリル位メチンプロトン、シクロアルカンの C2 位の側鎖の C2’位のプロトンにそれぞれ 3.2%、1.5%の NOE が観測された。環のアリル位メチレンプロトンには NOE は観測されなかった。**2d** の立体化学も同様に NOE の測定により決定した。メチル基への照射で環のアリル位のメチンプロトンに 2.3%の NOE が観測された。環のアリル位メチレンプロトンには NOE は観測されなかった。トリメチルシリル基のメチル基への照射で環のアリル位メチレンプロトンに 0.4%の NOE が観測された。この結果より、ジメチル亜鉛のメチル基は、アルキンとジエン部位の間に新たに形成される単結合に対してシス付加することが明らかになった。

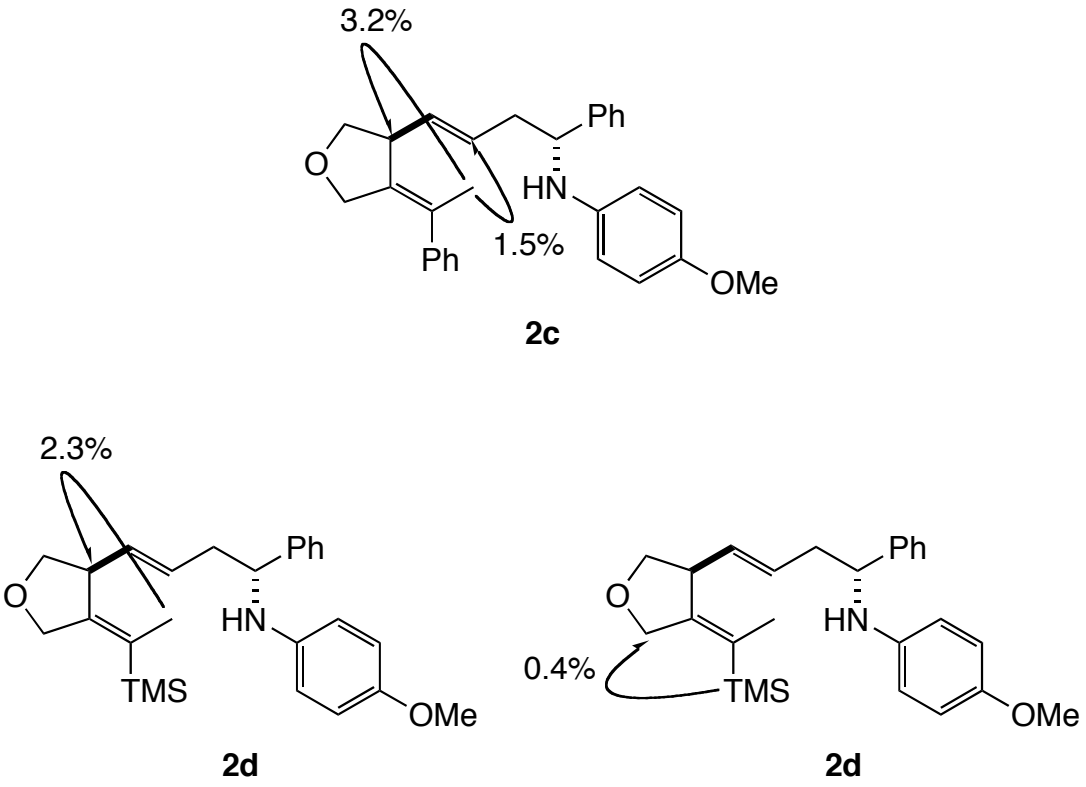
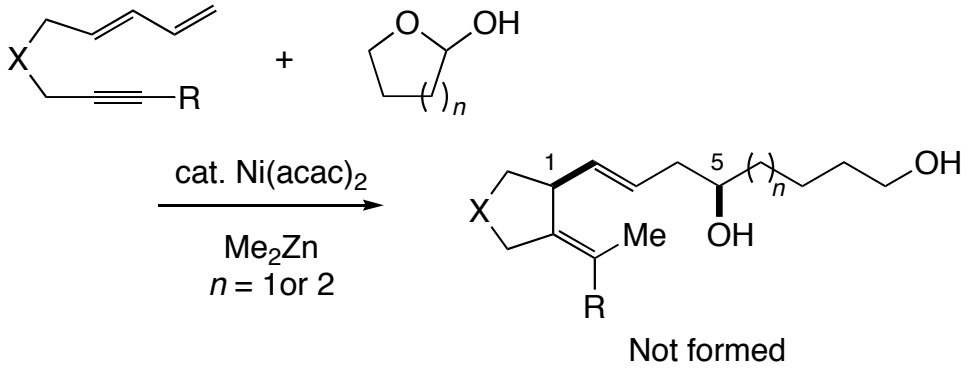


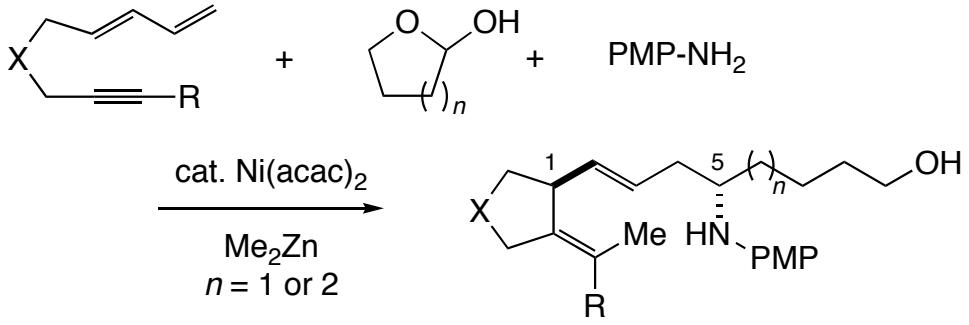
Figure 3. NOE Increment (%) Observed for **2c** and **2d**

４－２－２　ニッケル触媒を用いるジメチル亜鉛、１，ω－ジエンイン、*N*，*O*－アセタールの多成分連結反応

各種糖（フラノース、ピラノース）の基本骨格をなすラクトールは、ω－ヒドロキシアルデヒド等価体であり，反応がラクトールに適用できれば、基質の適用範囲を糖まで拡張でき、生成物に糖の立体化学を反映させたポリオールの合成が可能になる。ニッケル触媒、ジメチル亜鉛共存下、１，ω－ジエンインとラクトールを反応させたが四成分連結反応による生成物の単離には至らなかった（式６）。前節で述べた通り、同様の多成分連結反応において、アルドイミンの方がアルデヒドよりも反応性が高いという知見を基に、系中でラクトールと *p*－アニシジンから *N*，*O*－アセタールを生成し、ニッケル触媒、ジメチル亜鉛共存下、１，ω－ジエンインと反応させると、期待通りに反応が進行し、１，５位の相対立体配置が *anti* 体のジエニルアミノアルコールを高収率で与えた（式７）。[6]　本節では、*N*，*O*－アセタールを用いた多成分連結反応の反応性、選択性について報告する。



(6)



(7)

１，ω－ジエンインの検討を行った。常圧窒素雰囲気下、ラクトール **6d**（1 mmol）と *p*－アニシジン（2 mmol）を THF（2 ml）中、室温で 12 時間反応させ、*N*，*O*－アセタールを生成した。それに、THF（1 ml）に溶解させたニッケルアセチルアセトナト（0.05 mmol）を cannula 法によって添加し、１，ω－ジエンイン（0.5 mmol）、ジメチル亜鉛 1M ヘキサン溶液（3.6 ml）を順に加えて反応を行った。その結果を Table 5 に示す。

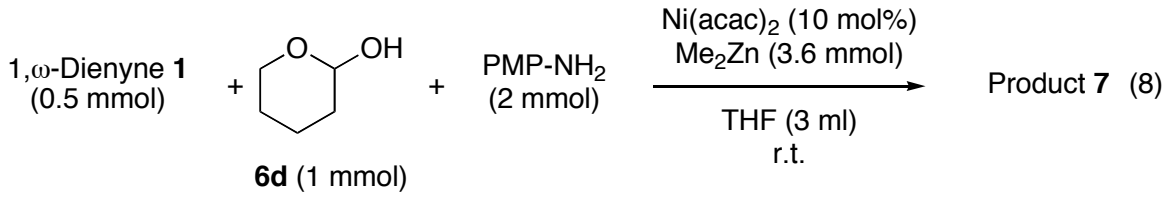
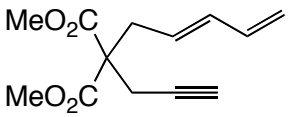
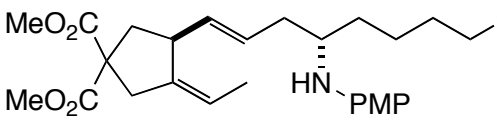
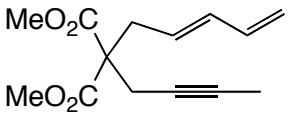
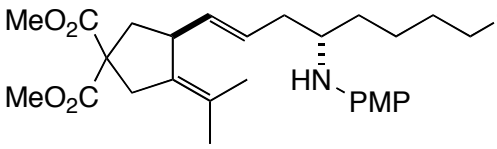
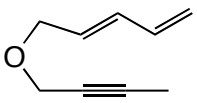
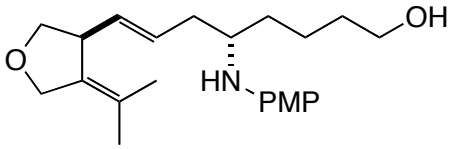
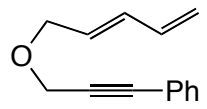
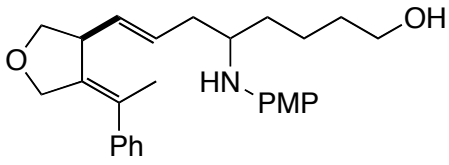
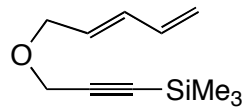
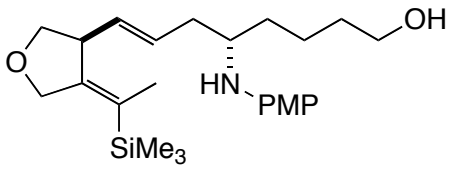
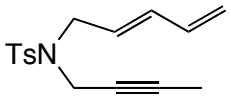
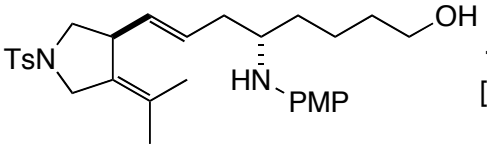
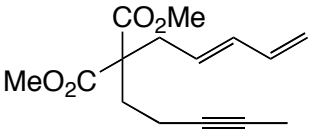
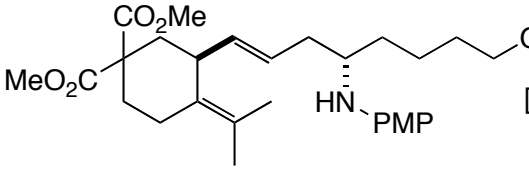
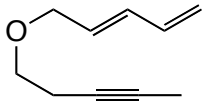
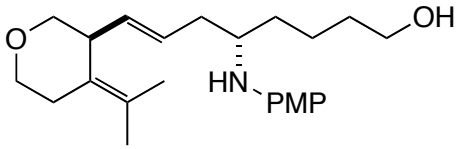
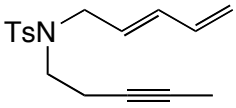
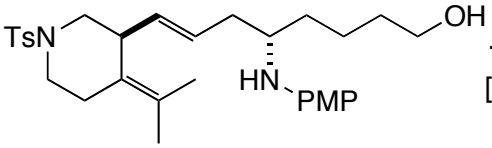


Table 5. Nickel-Catalyzed Conjugative Addition of Me_2Zn toward *N,O*-Acetals Across 1,ω-Dienynes **1**: Formation of Five and Six-Membered Ring Compounds.[a]

Run	1,ω-Dienyne **1**	Time (h)	% Isolated yield of product **7**
1	 **1i**	2	 **7i**: 27 [single]
2	 **1a**	3	 **7a**: 73 [single]
3	 **1b**	3	 **7b**: 89 [single]

(Table 5 continued.)

4	 **1c**	1		**7c**: 65 [single]
5	 **1d**	1		**7d**: 65 [single]
6	 **1e**	3		**7e**: 85 [single]
7	 **1f**	2		**7f**: 61 [single]
8	 **1g**	2		**7g**: 67 [single]
9	 **1h**	2[b]		**7h**: 78 [single]

[a] Reaction conditions: Lactol **6d** (1 mmol) and *p*-methoxyaniline (2 mmol) in THF (1.5 ml) at room temperature over night, and then $Ni(acac)_2$ (0.05 mmol) dissolved in THF (1.5 ml), a 1,ω-Dienyne **1** (0.5 mmol), Me_2Zn (3.6 mmol in hexane) at room temperature under N_2 for the period of time indicated.[b] At 50 ºC. PMP = *p*-methoxyphenyl. Ts = *p*-toluenesulfonyl.

末端アルキン **1i** を用いると、ジメチル亜鉛、アルキン、ジエン、*N*, *O*－アセタールの五成分連結反応が位置および立体選択的に進行し、低収率であるが **7i** を与えた（Run 1）。内部アルキンの方が末端アルキンよりも反応性が良く、**1i** の場合よりも収率の向上が見られ、シクロペンタン誘導体 **7a**、テトラヒドロフラン誘導体 **7b**-**7d**、ピロリジン誘導体 **7e** を高収率、かつ単一のジアステレオマーで与えた（Runs 2-6）。アルキンにフェニル基、立体的に嵩高いトリメチルシリル基が置換した **1c**、**1d** も同様の反応性を示した（Runs 4 and 5）。主鎖の炭素数が一つ増えた **1f**、**1g**、**1h** を用いても、速やかに反応は進行し、良好な収率でシクロヘキサン誘導体 **7f**、テトラヒドロピラン誘導体 **7g**、ピペリジン誘導体 **7h** が単一生成物で得られた（Runs 7-9）。

種々のラクトールと *p*－アニシジンから生成した *N*，*O*－アセタールを用いて反応を行った。常圧窒素雰囲気下、ラクトール（1 mmol）と *p*－アニシジン（2 mmol）を THF（2 ml）中、室温で 12 時間反応させ、*N*，*O*－アセタールを生成した。それに、THF（1 ml）に溶解させたニッケルアセチルアセトナト（0.05 mmol）を cannula 法によって添加し、１，ω－ジエンイン **1a**（0.5 mmol）、ジメチル亜鉛 1M ヘキサン溶液（3.6 ml）を順に加えて反応を行った。その結果を Table 6 に示す。

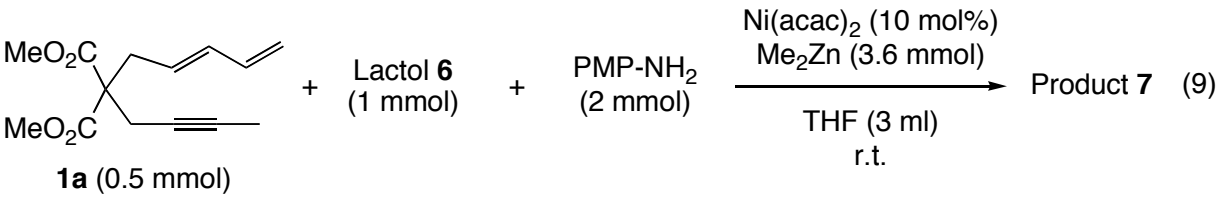
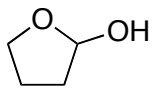
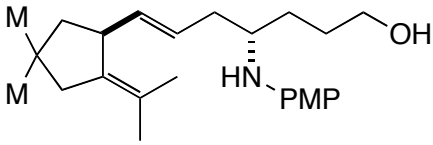
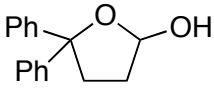
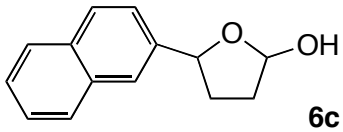
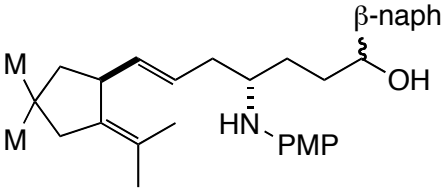
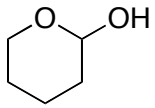
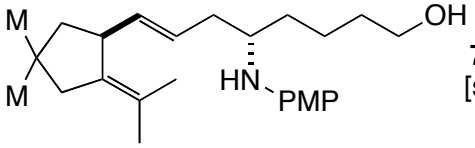
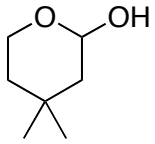
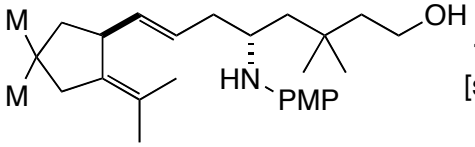
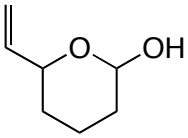
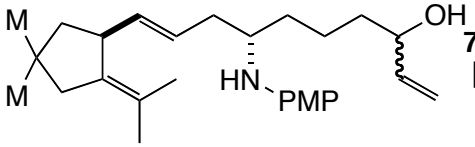
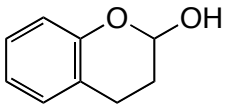
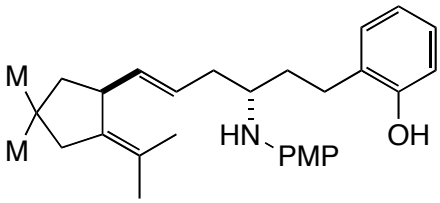
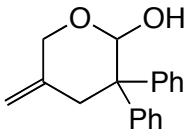
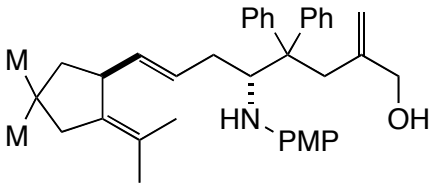
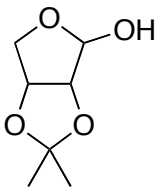
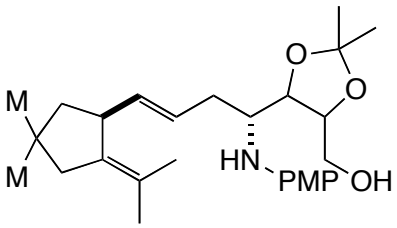


Table 6. Nickel-Catalyzed Conjugative Addition of Me_2Zn toward *N,O*-Acetals Across 1,ω-Dienyne **1a**[a]

Run	Lactol **6**	Time (h)	% Isolated yield of product **7** [Diastereomer ratio]
1	 **6a**	3	 **7j**: 61 [single]
2	 **6b**	2	Complex mixture
3	 **6c**	1	 **7k**: 85 [1 : 1][b]

(Table 6, continued.)

4		**6d**	3		**7a**: 73 [single]
5		**6e**	1		**7*l***: 80 [single]
6		**6f**	0.5		**7m**: 91 [4 : 1]
7		**6g**	0.5		**7n**: 86 [9 : 1]
8		**6h**	0.5		**7o**: 10
9		**6i**	1		**7p**: 80 [10 : 1]

[a] Reaction condition: Lactol (1 mmol) and *p*-methoxyaniline (2 mmol) in THF (1.5 ml) were reacted at room temperature for 12 h under N_2, and then $Ni(acac)_2$ (0.05 mmol) was dissolved in THF (1.5 ml), 1,ω-Dienyne **1a** (0.5 mmol), Me_2Zn (3.6 mmol, 1 M hexane) at room temperature under N_2 for the period of time indicated. PMP = *p*-methoxyphenyl. M and Ts stand for CO_2Me and *p*-toluenesulfonyl. [b] Diastereoisomers arising from the configrational isomerism of the carbon bearing the OH group.

五員環ラクトール **6a** を用いて反応を行うと、良好な収率で単一のジエニルアミノアルコール **7j** を与えた（Run 1）。**6b** を用いた場合、反応が複雑になり、生成物の単離には至らなかった（Run 2）。**6c** を用いた場合には、１，５－ジアスレオ選択的に反応は進行したが、二種類のジアステレオマーを１：１の割合で与えた（Run 3）。六員環ラクトールの場合も、速やかに五成分連結反応が進行した（Runs 4-7）。**6d**、**6e** を用いて反応を行うと、高収率で環化生成物 **7a**、**7*l*** を与え、生成物の立体化学は単一であった（Runs 4 and 5）。**6f** を用いて反応を行うと、Run 3 の結果と同様に、１，５－ジアステレオ選択的に反応は進行したが、二種類のジアステレオマーの混合物を与えた（Run 6）。**6g** を用いて反応を行うと、他の六員環ラクトールを用いた反応と比べて、１，５－ジアステレオ選択性の低下が見られたが、高収率で **7n** を与えた（Run 7）。**6h** を用いた場合には、低収率で **7o** を与える結果となった（Run 8）。エリトロース誘導体 **6i** を用いても高収率で **7p** を与えた（Run 9）。

六員環ラクトール **6d** と各種アミンから生成した *N, O*－アセタールを用いて反応を行った。常圧窒素雰囲気下、ラクトール **6d**（1 mmol）と各種アミン（2 mmol）を THF（2 ml）中、室温で 12 時間反応させ、*N, O*－アセタールを生成した。それに、THF（1 ml）に溶解させたニッケルアセチルアセトナト（0.05 mmol）を cannula 法によって添加し、１，ω－ジエンイン **1a**（0.5 mmol）、ジメチル亜鉛 1M ヘキサン溶液（3.6 ml）を順に加えて反応を行った。その結果を Table 7 に示す。

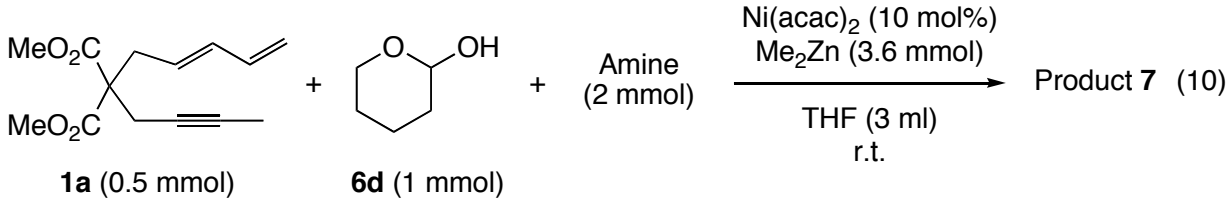
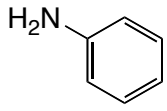
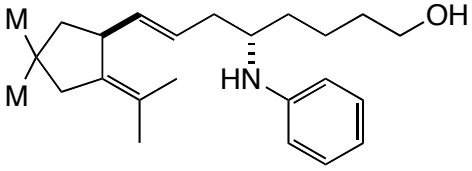
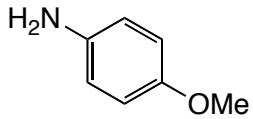
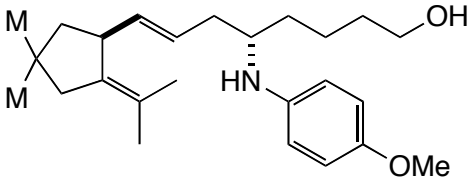
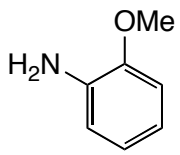
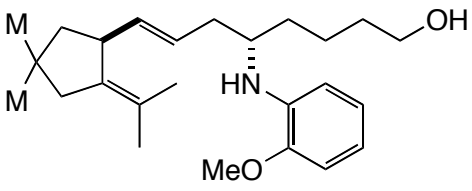
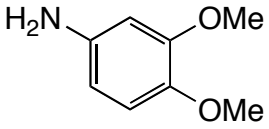
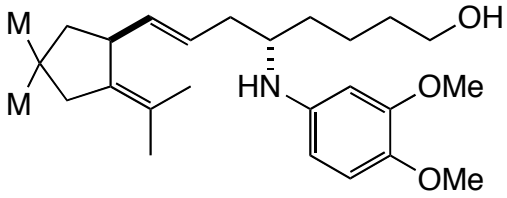
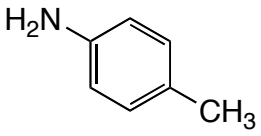
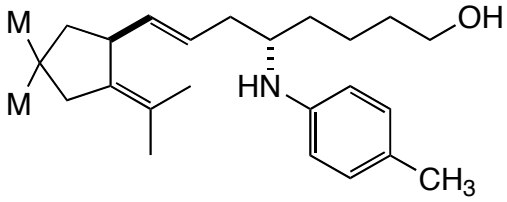
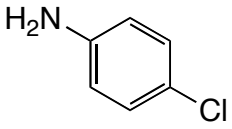
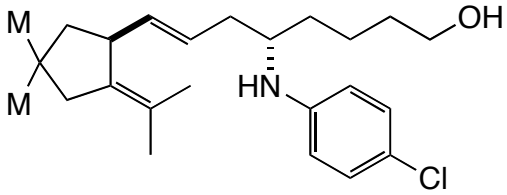
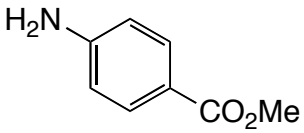
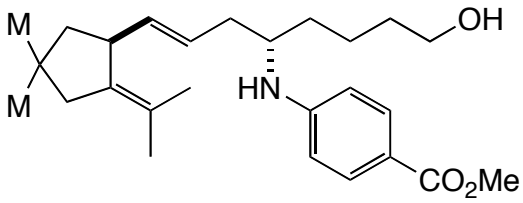
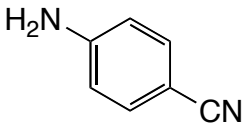
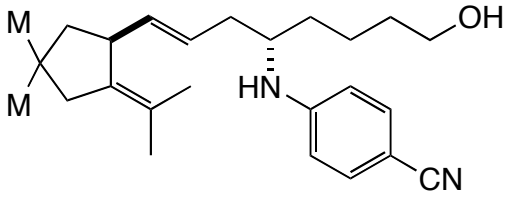
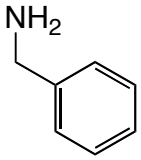
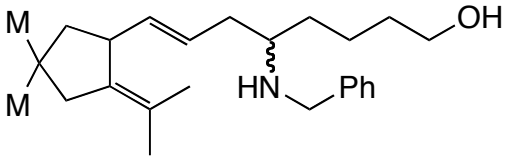


Table 7. Nickel-Catalyzed Conjugative Addition of Me_2Zn toward *N,O*-Acetals Across 1,ω-Dienyne **1a**[a]

Run	Amine	Time (h)	% Isolated yield of product **7** [Diastereomer ratio]
1[a]		3	 **7q**: 84 [single]
2[a]		1	 **7a**: 73 [single]
3[a]		0.5	 **7r**: 38 [single]

(Table 7, continued.)

4[a]		0.5		**7s**: 88 [single]
5[a]		0.5		**7t**: 73 [single]
6[a]		3		**7u**: 83 [single]
7[a]		0.5		**7v**: 67 [single]
8[a]		4		**7w**: 54 [single]
9[b]		25		**7x**: 74 [1 : 1]

[a] Reaction condition: Lactol **6d** (1 mmol) and an amine (2 mmol) in THF (1.5 ml) were reacted at room temperature for 12 h under N_2, and then $Ni(acac)_2$ dissolved in THF (1.5 ml), 1,ω-Dienyne **1a** (0.5 mmol), Me_2Zn (3.6 mmol, 1 M hexane) at room temperature under N_2 for the period of time indicated.
[b] Reaction condition: Lactol **6d** (1 mmol) and an amine (2 mmol) in THF (2 ml) were reacted at reflux for 0.5 h; distillation THF (azeotropic removal of water) under N_2, and then $Ni(acac)_2$ (0.05 mmol) was dissolved in THF (3 ml), 1,ω-Dienye **1a** (0.5 mmol), Me_2Zn (3.6 mmol, hexane) at room temperature under N_2 for period of time indicated.
M stands for CO_2Me.

芳香族アミンのパラ位に電子供与基、電子吸引基を導入した *N, O*－アセタールは速やかに反応し、１，５－ジアステレオ選択的にジエニルアミノアルコールを与えた（Runs 2,4-6）。パラ位にエステル基、シアノ基が置換した芳香族アミンから生成した *N, O*－アセタールも速やかに反応し、良好な収率で環化生成物を与えた（Runs 7 and 8）。オルト位が置換した芳香族アミンから生成した *N, O*－アセタールを用いた場合には、環化生成物の収率が著しく低下した（Run 3）。ベンジルアミンから生成した *N, O*－アセタールを用いた場合、１，５－ジアステレオ選択性は発現しなかった（Run 9）。

有機亜鉛の検討を行った。常圧窒素雰囲気下、ラクトール **6d**（1 mmol）と *p*－アニシジン（2 mmol）を THF（2 ml）中、室温で 12 時間反応させ、*N*，*O*－アセタールを生成した。それに、THF（1 ml）に溶解させたニッケルアセチルアセトナト（0.05 mmol）を cannula 法によって添加し、１，ω－ジエンイン **1a**（0.5 mmol）、有機亜鉛（3.6 mmol）を順に加えて反応を行った。その結果を Table 8 に示す。

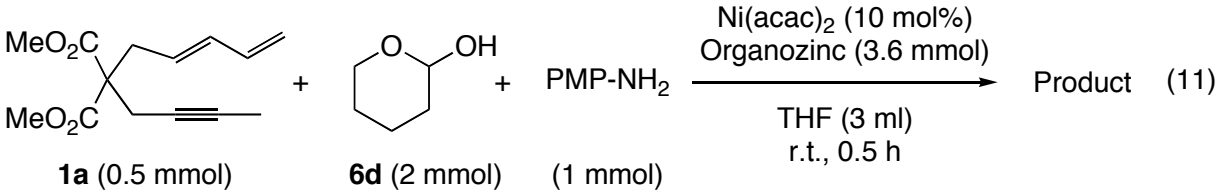
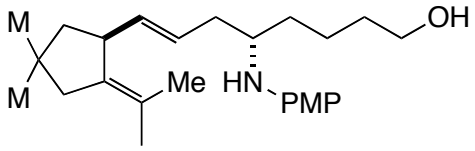
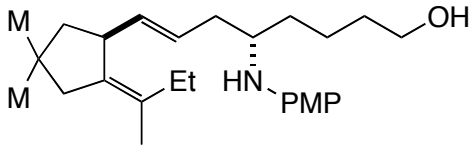
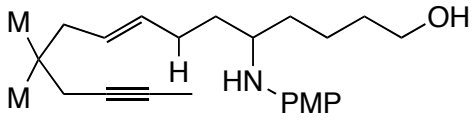
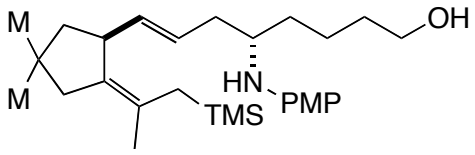


Table 8. Nickel-Catalyzed Coupling of Organozincs and *N,O*-Acetals Across 1,ω-Dienyne **1a**[a]

Run	Organozinc	Time (h)	% Isolated yield of product	
1	Me_2Zn	3		**7a** (73%) [single]
2	Et_2Zn	0.5		**8** (37%) [single]
				**9** (20%)
3	Ph_2Zn[b]	0.5	Complex mixture	
4	$(TMSCH_2)_2Zn$[c]	4		**10** (69%) [single]

[a] Reaction condition: Lactol **6d** (1 mmol) and *p*-methoxyaniline (2 mmol) in THF (1.5 ml) were reacted at room temperature for 12 h under N_2, and then $Ni(acac)_2$ (0.05 mmol) was dissolved in THF (1.5 ml), 1,ω-Dienyne **1a** (0.5 mmol), organozinc (3.6 mmol, 1 M hexane) at room temperature under N_2 for the period of time indicaded.
[b] Ph_2Zn [prepared from PhMgBr (7.2 mmol, in THF) and $ZnCl_2$ (3.6 mmol in ether)].
[c] $(TMSCH_2)_2Zn$ [prepared from $TMSCH_2MgCl$ (7.2 mmol, ether) and $ZnCl_2$ (3.6 mmol in ether)].
TMS and PMP stand for trimethylsilyl and *p*-methoxyphenyl group.

ジメチル亜鉛は、１，ω－ジエンイン **1a**、*N*，*O*－アセタールと五成分連結反応し、単一の環化生成物を良好な収率で与えた（Run 1）。β－水素を有するジエチル亜鉛を用いると、速やかに反応は完結し、五成分連結反応による **8** と ジエチル亜鉛，１，３－ジエン、*N*，*O*－アセタールのホモアリル化反応による **9** を与えた（Run 2）。ジフェニル亜鉛を用いた場合、反応が複雑になり、環化生成物の単離には至らなかった（Run 3）。$(TMSCH_2)_2Zn$ を用いても反応は進行し、分子内にアリルシランを有する **10** を良好な収率で与えた（Run 4）。

N，*O*－アセタールの多成分連結反応によって得られた環化生成物を *p*－ブロモ安息香酸エステルに誘導すると結晶性が良い生成物 **11** が得られた。単結晶 X－線構造解析によりその立体構造を決定した（Figure 4）。[10] その結果、環状のアリル位メチン炭素に結合した側鎖と、その側鎖のアミノ基の１，５位の相対立体配置が *anti* 体であることが明らかになった。

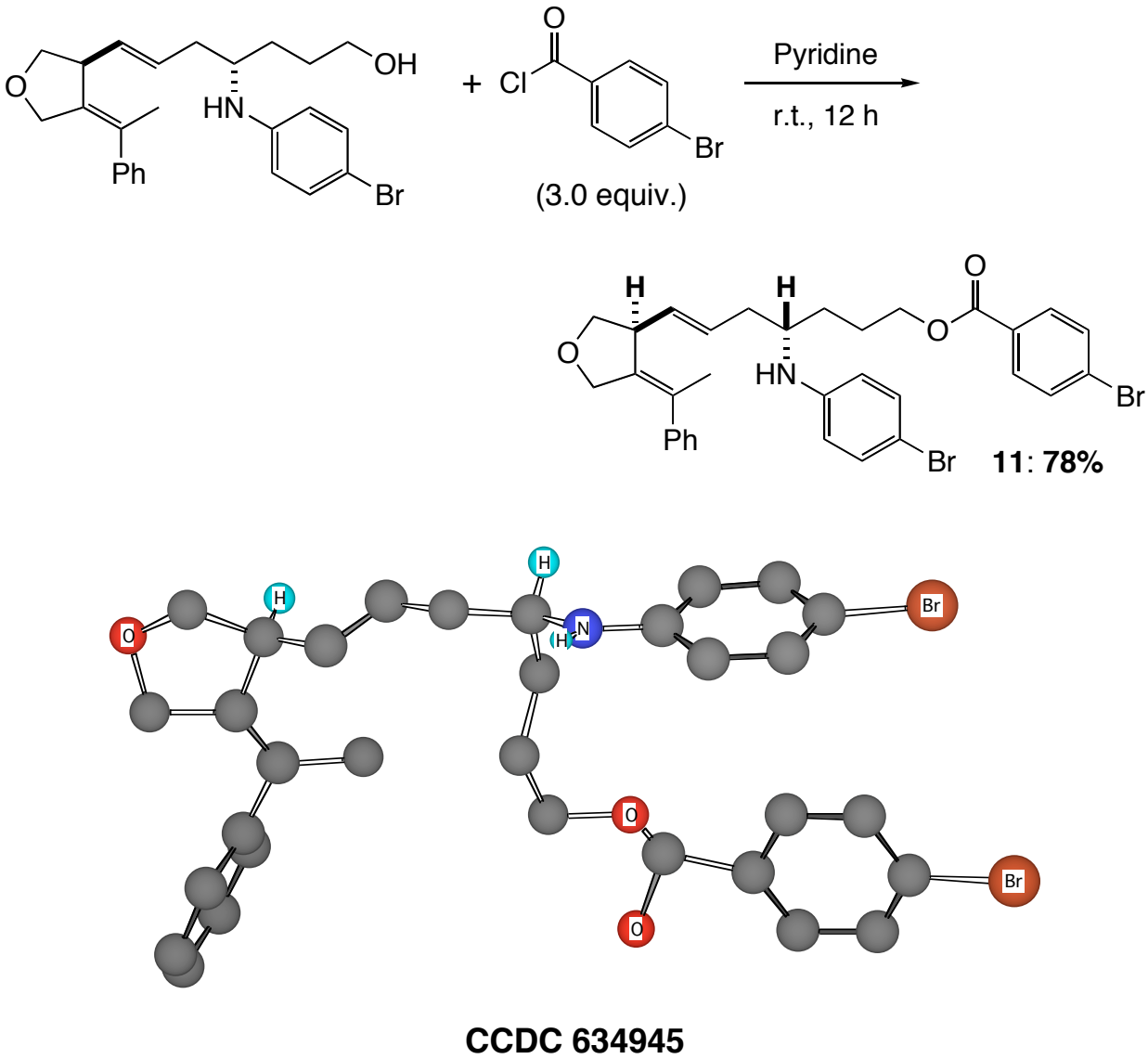
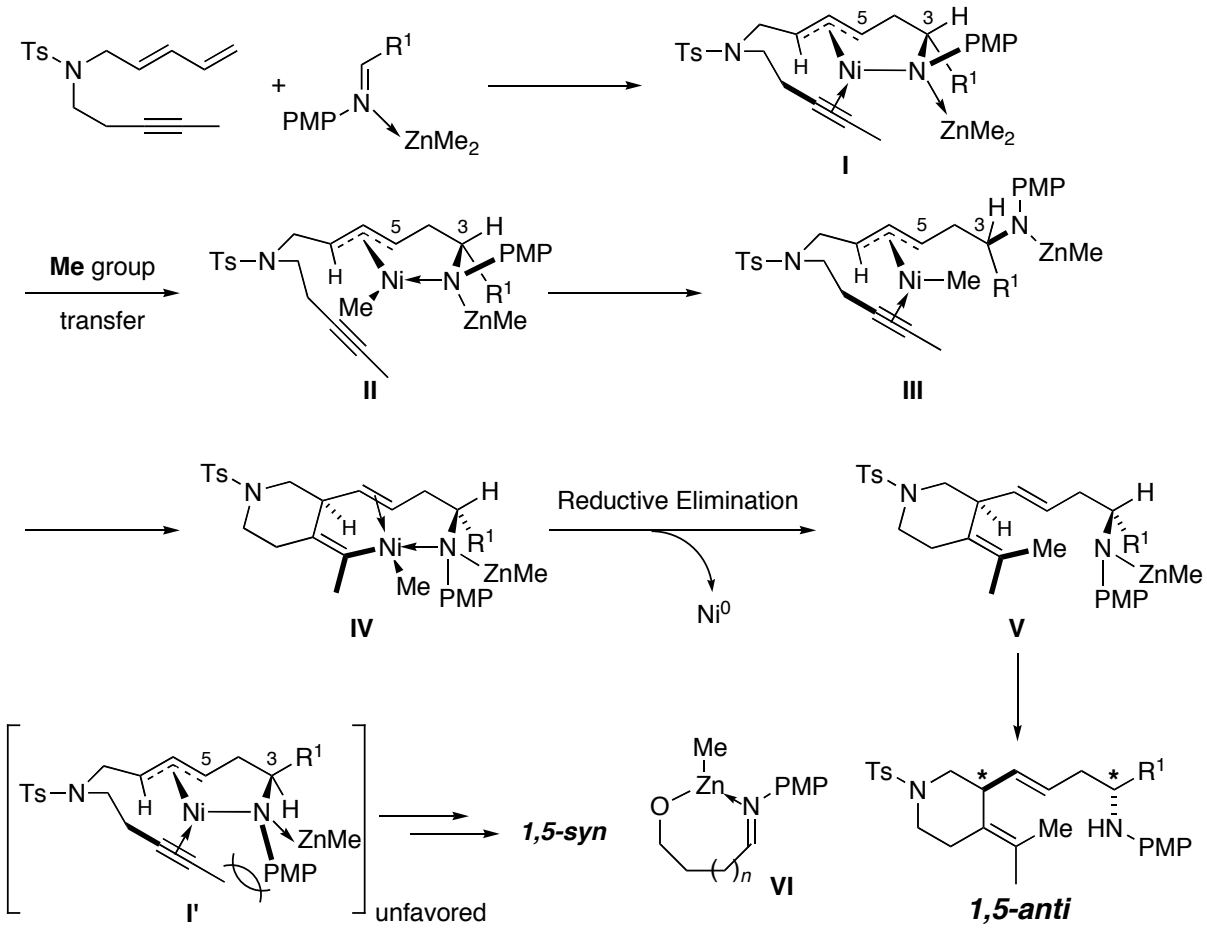


Figure 4. The Chem 3D^{TM} Presentation of X-Ray Structure of a *p*-Bromobenzoic Acid Ester **11**. For clarity, all protons except those on the stereogenic centers are omitted.

五成分連結反応における位置選択性及び立体選択性から判断して、次のような反応機構を想定した（Scheme 4）。



Scheme 4. Plausible Reaction Mechanism for the Nickel-Catalyzed Multi-Component Connection Reaction

Ni(0)が１，ω－ジエンインに配位してジエン部位が求核活性化する。また、ジメチル亜鉛がルイス酸として作用し、アルドイミンを親電子活性化する。ジエンとアルドイミンに対して Ni(0)の酸化的環化が進行し、アザニッケラサイクル中間体 **I** を形成する。１，５－*anti* 選択性は、中間体 **I** の構造に由来しいている可能性が高い。１，５－*syn* 体に導く中間体**I'**はアルドイミンの置換基R^1が擬エクアトリアル位に位置し、R^1 と C5 炭素が *anti* のコンホメーションであるが、Ni(II)が平面四角形型の配位をとるために､アルキンと窒素上の置換基との間で大きな立体反発が生じると考えられる。

一方、中間体 **I** では、R^1 と C5 炭素との間でゴーシュ反発が生じるが、この反発は中間体 **I'**のアルキンと窒素上の置換基との立体反発に比べて遥かに小さいと思われる。それゆえ、アザニッケラサイクル中間体 **I** を経由して反応が進行すると考えられる。次に、ジメチル亜鉛のメチル基がニッケルに転位して、アルキンがニッケルに配位した中間体 **III** を形成すると思われる。**III** のπ－アリルニッケル部位がアルキンに対してシス付加して、メチルビニルニッケル中間体 **IV** を形成し、還元的脱離が進行して、生成物を与えると同時に Ni(0)を再生する。このようにして反応が１，５－*anti* 選択的に進行するものと推定している。

本研究では、ニッケル触媒により、有機亜鉛，１，ω－ジエンイン、アルドイミンの多成分連結反応が環化を伴い、室温で速やかに進行し、単一のホモアリルアミンを高収率で与えることを見出した。本反応で最も重要なことは、前章で述べたアルデヒドの反応とは立体選択性が逆転し、１，５－*anti* ジアステレオ選択的に反応が進行することである。さらに重要な事柄として、アルドイミン生成の際に生じる水を取り除く必要がなく、そのまま反応に用いることができる。このような操作を省略できるという点でも、本反応は合成反応として優れている。詳細は不明であるが、系中に存在する過剰のアミン，水が反応を促進させる現象も興味深い。また、*N, O*－アセタールを用いても、１，５－*anti* ジアステレオ選択的に反応し、高収率でジエニルアミノアルコールを与える。Scheme 4 の **IV** に示すようなヒドロキシル基と窒素原子を介したキレート効果が反応性を高めていると考えられる。基質の適用範囲が糖へ拡張できれば、生成物に糖の立体化学を反映させたポリオールの合成が可能になり、機能性材料や生理活性物質創製の分野で強力な合成法となることが期待される。

Experimental Section

Reactions employed oven-dried glassware unless otherwise noted. Thin layer chromatography (TLC) employed glass 0.25 mm silica gel plates with UV indicator (Merck, Silica gel $60F_{254}$). Flash chromatography columns were packed with silica gel (Wakogel-C300) as a slurry in hexane. Flash chromatography was conducted eluting with a continuous gradient from hexane to the indicated solvent. Proton and carbon NMR data were obtained with a JEOL-GX400 with tetramethylsilane as an internal standard. Chemical shift values were given in ppm downfield from the internal standard. Infrared spectra were recorded with a JASCO A-100 FT-IR spectrophotometer. High resolution mass spectra (HRMS) were measured with a JEOL JMS-DX303.

Solvents and Reagents. Tetrahydrofuran was distilled from a blue solution of sodium benzophenone ketyl under N_2 immediately prior to use. $Ni(acac)_2$ (Aldrich), dimethylzinc (1.0 M solution in hexanes) (Kanto Kagaku Kogyo, Co., Ltd.), *p*-chlorobenzaldehyde, and *p*-anisidine (Tokyo Kasei Kogyo Co., Ltd.) were purchased and used without further purification. Benzaldehyde, furfral, dihydrocinnamaldehyde, cyclohexanecarboxyaldehyde, were purchased from Tokyo Kasei Kogyo Co., Ltd., and purified by distillation prior to use. Lactols were prepared according to the literature.[8,9]

Preparation of 5-(3-Trimethylsilyl-2-propynyloxy)-(1,3*E*)-pentadiene (**1d**): Into a round-bottom flask was placed NaH (480 mg; a 60% dispersion in oil, 12 mmol). The dispersion was washed with hexane (2 x 5 mL). Into the flask were added THF (30 mL), and was added dropwise a solution of 2-propyn-1-ol (0.67 g, 12 mmol) in 10 mL THF at 0 °C. The resulting mixture was stirred at room temperature for 1 h. This mixture was cooled again to 0 °C, and

into this a solution of l-chloro-2,4-pentadiene[5] (1.05 mL, 10 mmol) dissolved in THF (10 mL) was added dropwise. The resulting mixture was allowed to warm to ambient temperature, and stirred for 52 h. The mixture was poured into ice-water and extracted with ether (2 x 30 mL). The organic phase was washed with sat. NH_4C1 and with sat. $NaHCO_3$, and dried ($MgSO_4$). The solvent was removed *in vacuo* to give 5-(2-propynyloxy)-(1,3*E*)-pentadiene. Into a flask containing the crude 5-(2-propynyloxy)-(1,3*E*)-pentadiene was added THF (30 mL), and then *n*-BuLi (6.9 mL. 11 mmol; 1.6 M in hexane) was added dropwise via syringe at -78 ˚C. After stirring for 1 h, chlorotrimethylsilane (1.3 g, 12 mmol) was added dropwise at the same temperature, and the reaction mixture was stirred for 1 h. The mixture was poured into water and extracted with ether (2 x 30 mL). The combined organic extracts were washed with sat. NH_4Cl, sat. $NaHCO_3$, and sat. NaCl, and dried ($MgSO_4$). Solvent was removed *in vacuo* and the residue was purified by means of column chromatography over silica gel (hexane/ethyl acetate = 20/1, v/v) to give **1d** in 16% yield. Other 1,ω-dienynes (**1a**-**1c**, **1e**-**1h**) were also prepared under similar way.[5]

5-(3-Trimethylsilyl-2-propynyloxy)-(1,3*E*)-pentadiene (**1d**): IR (neat) 3086 (w), 2963 (m), 1605 (w), 1350 (m), 1250 (s), 1096 (s), 1003 (s), 849 (s), 764 (m) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.18 (s, 9 H), 4.10 (d, J = 6.1 Hz, 2 H), 4.14 (s, 2 H), 5.11 (d, J = 10.5 Hz, 1 H), 5.22 (d, J = 16.3 Hz, 1 H), 5.76 (dt, J = 14.6, 6.1 Hz, 1 H), 6.27 (dd, J = 14.6, 10.5 Hz, 1 H), 6.34 (dt, J = 16.3, 10.5 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 0.3, 58.3, 70.1, 91.8, 101.8, 118.1, 129.5, 134.3, 136.5; HRMS calcd for $C_{11}H_{18}OSi$: 194.1127. Found m/z (relative intensity) 194.1106 (M^+, 29), 193 (63), 179 (100).

General Procedure for the Ni-Catalyzed Coupling of Me_2Zn and Aldimine Across 1,ω-Dienyne (Table 5, Run 2): A mixture of *p*-anisidine (246 mg, 2 mmol) and 2-hydroxy-1-oxacyclohexane[8] (103 mg, 1 mmol) in dry THF (2 mL) was stirred at room temperature overnight under N_2. In a flask contaning $Ni(acac)_2$ (12.8 mg, 0.05 mmol) was purged with N_2

and into this flask were added successively THF (1 mL), the above-prepared solution (via cannula), dienyne **1a** (125 mg, 0.5 mmol), Me_2Zn (3.6 mL, 1 M hexane). The homogeneous solution was stirred at room temperature for 1 h; $R_{f\mathbf{1a}} = 0.7$, $R_{f\mathbf{7a}} = 0.07$ (hexane/EtOAc = 2:1 vol./vol.). The mixture was partitioned into EtOAc (20 mL)/H_2O (20 mL). The water phase was saturated with NaCl and extracted with EtOAc (2 x 10 mL). The combined organic phase was dried (K_2CO_3) and concentrated *in vacuo*. The residue was purified by column chromatography over silica gel (hexane/EtOAc gradient; 2:1 to 1:1 v/v) to give **7a** (171.3 mg) in 73% yield as colorless oil.

4,4-Dimethoxycarbonyl-2-[4-(*p*-anisidyl)-8-hydroxy-(1*E*)-octenyl]-1-isopropylidenecyclopentane (**7a**): IR (neat) 3395 (m), 2932 (w), 1736 (s), 1512 (s), 1443 (s), 1242 (s), 1042 (s), 818 (s), 733 (w) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.41 – 1.60 (m, 6 H), 1.57 (s, 3 H), 1.65 (s, 3 H), 2.06 (dd, *J* = 5.9, 13.2 Hz, 1 H), 2.18 – 2.22 (m, 2 H), 2.57 (dd, *J* = 8.5, 13.2 Hz, 1 H), 2.83 – 2.92 (m, 2 H), 3.28 (ddm, *J* = 5.9, 8.5 Hz, 1 H), 3.30 (m, 1 H), 3.63 (t, *J* = 6.3 Hz, 2 H), 3.70 (s, 3 H), 3.71 (s, 3 H), 3.74 (s, 3 H), 5.31 (dm, *J* = 15.1 Hz, 1 H), 5.36 (dm, *J* = 15.1 Hz, 1 H), 6.55 (br d, *J* = 8.5 Hz, 2 H), 6.75 (d, *J* = 8.5 Hz, 2 H); ^1H NMR (400 MHz, THF-d_8) δ 1.32 – 1.56 (m, 6 H), 1.57 (s, 3 H), 1.63 (s, 3 H), 2.00 (dd, *J* = 6.2, 13.1 Hz, 1 H), 2.13 (dt, *J* = 13.7, 6.8 Hz, 1 H), 2.18 (dt, *J* = 13.7, 7.6 Hz, 1 H), 2.53 (dd, *J* = 8.4, 13.1 Hz, 1 H), 2.83 (br d, *J* = 16.6 Hz, 1 H), 2.89 (br d, *J* = 16.6 Hz, 1 H), 3.22 (br dd, *J* = 6.2, 7.6 Hz, 1 H), 3.28 (br d, *J* = 8.4 Hz, 1 H), 3.40 – 3.50 (m, 2 H), 3.61 (s, 3 H), 3.62 (s, 3 H), 3.63 (s, 3 H), 3.93 (br s, 1 H), 5.28 (dd, *J* = 7.6, 14.9 Hz, 1 H), 5.41 (dt, *J* = 14.9, 6.8 Hz, 1 H), 6.47 (d, *J* = 9.0 Hz, 2 H), 6.64 (d, *J* = 9.0 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.8, 21.6, 22.2, 32.7, 33.9, 36.7, 38.7, 41.2, 44.2, 52.6, 54.1, 55.8, 59.1, 62.7, 114.9, 125.2, 125.9, 132.9, 135.8, 152.0, 172.1, 172.2; HRMS calcd for $C_{27}H_{39}NO_6$: 473.2777. Found *m*/*z* (relative intensity) 474 (M^++1, 32), 473.2770 (M^+, 100), 472 (7), 456 (2), 442 (13).

(2*S,4'*R**)-4,4-Dimethoxycarbonyl-2-[4-(*p*-anisidyl)-4-phenyl-(1*E*)-butenyl]-1-isopropylidenecyclopentane** (**2a**): IR (neat) 3395 (w), 2909 (m), 1736 (s), 1512 (s), 1435 (m), 1242 (s), 1042 (m), 818 (m) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.53 (s, 3 H), 1.64 (s, 3 H), 2.11 (dd, *J* = 5.6, 13.2 Hz, 1 H), 2.38 (dt, *J* = 14.2, 7.6 Hz, 1 H), 2.51 (dt, *J* = 14.2, 5.7 Hz, 1 H), 2.57 (dd, *J* = 9.2, 13.2 Hz, 1 H), 2.87 (br d, *J* = 16.2 Hz, 1 H), 2.96 (br d, *J* = 16.2 Hz, 1 H), 3.32 (ddm, *J* = 5.6, 9.2 Hz, 1 H), 3.66 (s, 3 H), 3.69 (s, 3 H), 3.70 (s, 3 H), 3.95 (br s, 1 H), 4.24 (dd, *J* = 5.7, 7.6 Hz, 1 H), 5.28 (dm, *J* = 15.1 Hz, 1 H), 5.41 (dm, *J* = 15.1 Hz, 1 H), 6.43 (d, *J* = 8.9 Hz, 2 H), 6.65 (d, *J* = 8.9 Hz, 2 H), 7.18 - 7.40 (m, 5 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.9, 21.5, 38.7, 41.1, 41.9, 44.1, 52.7, 55.7, 58.2, 59.2, 114.5, 114.7, 125.5, 126.1, 126.2, 126.7, 128.4, 132.6, 136.2, 141.7, 143.8, 151.8, 172.1; HRMS calcd for $C_{29}H_{35}NO_5$: 477.2515. Found *m/z* (relative intensity) 478 (M^++1, 32), 477.2507 (M^+, 100).

(4*S,4'*R**)-3-Isopropylidene-4-[4-(*p*-anisidyl)-4-phenyl-(1*E*)-butenyl]tetrahydrofuran** (**2b**): IR (neat) 3387 (w), 2909 (m), 2839 (m), 2361 (s), 1620 (w), 1512 (s), 1450 (m), 1242 (s), 1049 (m), 972 (w), 756 (m) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.58 (s, 3 H), 1.63 (s, 3 H), 2.43 (dt, *J* = 14.2, 7.3 Hz, 1 H), 2.55 (dt, *J* = 14.2, 7.3 Hz, 1 H), 3.29 (ddm, *J* = 2.9, 6.2 Hz, 1 H), 3.64 (s, 3 H), 3.71 (dd, *J* = 2.9, 8.5 Hz, 1 H), 3.86 (dd, *J* = 6.2, 8.5 Hz, 1 H), 4.22 (t, *J* = 7.3 Hz, 1 H), 4.25 (dm, *J* = 12.7 Hz, 1 H), 4.32 (dm, *J* = 12.7 Hz, 1 H), 5.36 (dt, *J* = 15.1, 7.3 Hz, 1 H), 5.54 (dd, *J* = 7.3, 15.1 Hz, 1 H), 6.41 (d, *J* = 9.0 Hz, 2 H), 6.66 (d, *J* = 9.0 Hz, 2 H), 7.20 – 7.33 (m, 5 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.2, 21.0, 21.1, 41.7, 45.6, 55.7, 58.3, 60.3, 70.1, 74.7, 114.5, 114.6, 123.4, 125.8, 126.3, 126.7, 128.3, 133.8, 134.3, 141.4, 143.6, 151.8; HRMS calcd for $C_{24}H_{29}NO_2$: 363.2198. Found *m/z* (relative intensity) 364 (M^++1, 30), 363.2199 (M^+, 100).

(4*S,4'*R**)-3-[(1*Z*)-Phenylethylidene]-4-[4-(*p*-anisidyl)-4-phenyl-(1*E*)-butenyl]tetrahydrofuran** (**2c**): IR (neat) 3387 (w), 2909 (w), 1514 (s), 1238 (s), 1036 (s), 820

(m), 762 (s), 702 (s) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.97 (br s, 3 H), 2.56 – 2.64 (m, 2 H), 3.47 (m, 1 H), 3.68 (s, 3 H), 3.71 (dm, *J* = 8.8 Hz, 1 H), 3.97 (dm, *J* = 8.8 Hz, 1 H), 4.12 (br d, *J* = 13.2 Hz, 1 H), 4.31 (m, 1 H), 4.33 (br d, *J* = 13.2 Hz, 1 H), 5.48 (dm, *J* = 15.0 Hz, 1 H), 5.61 (dm, *J* = 15.0 Hz, 1 H), 6.47 (br d, *J* = 8.8 Hz, 2 H), 6.67 (dm, *J* = 8.8 Hz, 2 H), 7.10 (d, *J* = 7.0 Hz, 2 H), 7.20 - 7.38 (m, 8 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.8, 41.5, 46.2, 55.8, 58.6, 70.6, 74.3, 114.9, 126.6, 126.8, 127.1, 128.3, 128.6, 129.5, 133.7, 137.5, 143.3, 152.3; HRMS calcd for $C_{21}H_{31}NO_2$: 425.2355. Found *m/z* (relative intensity) 426 (M^++1, 30), 425.2342 (M^+, 100).

(4*S,4'*R**)-3-[(1*Z*)-Trimethylsilylethylidene]-4-[4-(*p*-anisidyl)-4-phenyl-(1*E*)-butenyl]tetrahydrofuran** (**2d**): IR (neat) 3387 (m), 3024 (m), 2955 (m), 2839 (s), 1512 (s), 1450 (m), 1242 (s), 1033 (m), 840 (s), 756 (s), 702 (s) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.08 (s, 9 H), 1.56 (br s, 1 H), 1.68 (s, 3 H), 2.46 (br dd, *J* = 13.9, 7.3 Hz, 1 H), 2.55 (br dd, *J* = 13.9, 7.3 Hz, 1 H), 3.42 (m, 1 H), 3.68 (s, 3 H), 3.70 (dm, *J* = 8.8 Hz, 1 H), 3.84 (dm, *J* = 8.8 Hz, 1 H), 4.22 (dm, *J* = 12.9 Hz, 1 H), 4.27 (dm, *J* = 7.3 Hz, 1 H), 4.34 (dm, *J* = 12.9 Hz, 1 H), 5.35 (dt, *J* = 15.2, 7.3 Hz, 1 H), 5.53 (dd, *J* = 15.2, 7.3 Hz, 1 H), 6.41 (d, *J* = 8.8 Hz, 2 H), 6.67 (d, *J* = 8.8 Hz, 2 H), 7.18 – 7.34 (m, 5 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ –0.8, 18.8, 41.6, 46.5, 55.7, 58.1, 70.8, 73.7, 114.6, 114.7, 126.1, 126.7, 128.3, 133.6, 141.4, 143.5, 149.9, 151.9; HRMS calcd for $C_{26}H_{35}NO_2Si$: 421.2437. Found *m/z* (relative intensity) 422 (M^++1, 35), 421.2434 (M^+, 100), 420 (3), 406 (18).

(4*S,4'*R**)-3-Isopropylidene-4-[4-(*p*-anisidyl)-4-phenyl-(1*E*)-butenyl]-*N*-(*p*-toluenesulfonyl)pyrrolidine** (**2e**): IR (neat) 3402 (w), 2916 (w), 1521 (s), 1342 (s), 1242 (s), 1165 (s), 1096 (m), 1042 (m), 817 (m), 664 (m) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.51 (s, 3 H), 1.54 (s, 3 H), 2.39 (br dd, *J* = 7.3, 13.7 Hz, 1 H), 2.42 (s, 3 H), 2.48 (dt, *J* = 13.7, 5.7 Hz, 1 H), 3.09 (dm, *J* = 9.0 Hz, 1 H), 3.25 (dm, *J* = 7.2 Hz, 1 H), 3.29 (dm, *J* = 9.0 Hz, 1 H), 3.56

(d, *J* = 13.4 Hz, 1 H), 3.68 (s, 3 H), 3.88 (d, *J* = 13.4 Hz, 1 H), 4.24 (dd, *J* = 5.7, 7.3 Hz, 1 H), 5.29 (dt, *J* = 15.4, 5.7 Hz, 1 H), 5.41 (dd, *J* = 7.2, 15.4 Hz, 1 H), 6.43 (br d, *J* = 8.8 Hz, 2 H), 6.67 (d, *J* = 8.8 Hz, 2 H), 7.21 – 7.29 (m, 5 H), 7.31 (d, *J* = 8.2 Hz, 2 H), 7.70 (d, *J* = 8.2 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.4, 21.1, 21.5, 41.5, 44.0, 50.3, 54.3, 55.7, 58.2, 114.7, 126.2, 126.3, 126.8, 127.8, 128.4, 129.5, 129.8, 132.6, 133.5, 143.4, 152.3; HRMS calcd for $C_{31}H_{36}N_2O_3S$: 516.2447. Found *m/z* (relative intensity) 517 (M^++1, 37), 516.2446 (M^+, 100), 515 (4).

(2*S,4'*R**)-4,4-Dimethoxycarbonyl-2-[4-(*p*-anisidyl)-4-phenyl-(1*E*)-butenyl]-1-isopropylidenecyclohexane (2f)**: IR (neat) 3402 (s), 2947 (s), 1736 (s), 1512 (s), 1450 (s), 1234 (s), 1042 (s), 826 (s), 702 (s) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.54 (s, 3 H), 1.62 (dm, *J* = 14.2 Hz, 1 H), 1.63 (s, 3 H), 2.18 (dm, *J* = 14.2 Hz, 1 H), 2.28 (m, 1 H), 2.34 – 2.46 (m, 3 H), 2.50 – 2.60 (m, 2 H), 3.46 (br s, 1 H), 3.66 (s, 3 H), 3.68 (s, 3 H), 3.73 (s, 3 H), 4.27 (dd, *J* = 4.8, 7.2 Hz, 1 H), 5.51 (dm, *J* = 15.4 Hz, 1 H), 5.47 (dm, *J* = 15.4 Hz, 1 H), 6.53 (d, *J* = 8.9 Hz, 2 H), 6.65 (d, *J* = 8.9 Hz, 2 H), 7.18 (m, 1 H), 7.23 – 7.38 (m, 4 H): ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.8, 20.0, 22.3, 31.5, 36.0, 38.5, 41.9, 52.4, 52.5, 52.6, 55.7, 58.2, 114.6, 114.7, 125.2, 125.4, 126.6, 128.3, 128.4, 135.2, 141.5, 143.6, 151.8, 172.2, 172.5; HRMS calcd for $C_{30}H_{37}NO_5$: 491.2672. Found *m/z* (relative intensity) 492 (M^++1, 33), 491.2665 (M^+, 100), 460 (9).

(2*S,4'*R**)-4-Isopropylidene-3-[4-(*p*-anisidyl)-4-phenyl-(1*E*)-butenyl]tetrahydropyran (2g)** (CCDC-209610)[10]: IR (neat) 3364 (m), 2963 (m), 2855 (m), 1512 (s), 1450 (w), 1234 (m), 1096 (m), 1042 (m), 964 (m), 818 (m), 702 (m) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.65 (s, 3 H), 1.67 (s, 3 H), 2.25 (m, 1 H), 2.36 (br d, *J* = 12.7 Hz, 1 H), 2.41 (ddm, *J* = 13.9, 7.8 Hz, 1 H), 2.55 (ddm, *J* = 13.9, 5.2 Hz, 1 H), 3.18 (dm, *J* = 6.6 Hz, 1 H), 3.30 (ddm, *J* = 10.7, 12.7 Hz, 1 H), 3.50 (dm, *J* = 11.1 Hz, 1 H), 3.67 (s, 3 H), 3.92 (d, *J* = 11.1 Hz, 1 H), 3.98 (dd, *J* = 5.2,

10.7 Hz, 1 H), 4.25 (dd, *J* = 5.2, 7.8 Hz, 1 H), 5.38 (ddm, *J* = 15.4, 6.6 Hz, 1 H), 5.80 (dd, *J* = 6.6, 15.4 Hz, 1 H), 6.41 (d, *J* = 8.8 Hz, 2 H), 6.65 (d, *J* = 8.8 Hz, 2 H), 7.15 - 7.40 (m, 5 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.5, 19.8, 27.0, 41.8, 42.2, 55.7, 58.2, 68.7, 72.8, 114.5, 114.6, 124.6, 126.1, 126.2, 126.6, 127.3, 128.3, 135.0, 141.7, 143.9, 151.7; HRMS calcd for $C_{25}H_{31}NO_2$: 377.2355. Found *m/z* (relative intensity) 378 (M^++1, 32), 377.2352 (M^+, 100), 376 (2).

(2*S,4'*R**)-4-Isopropylidene-3-[4-(*p*-anisidyl)-4-phenyl-(1*E*)-butenyl]-*N*-(*p*-toluenesulfonyl)piperidine (2h)**: IR (neat) 3395 (w), 2916 (m), 1512 (s), 1458 (m), 1335 (s), 1242 (s), 1165 (s), 1103 (m), 1034 (m), 934 (m), 818 (s), 756 (m), 702 (m) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.59 (s, 3 H), 1.60 (s, 3 H), 2.08 – 2.28 (m, 2 H), 2.33 (dm, *J* = 11.2 Hz, 1 H), 2.38 – 2.50 (m, 2 H), 2.40 (s, 3 H), 2.54 (dtm *J* = 6.3 Hz, 1 H), 3.36 (m, 1 H), 3.68 (s, 3 H), 3.74 (br d, *J* = 11.2 Hz, 1 H), 3.78 (m, 1 H), 4.01 (br s, 1 H), 4.27 (dm, *J* = 7.6 Hz, 1 H), 5.40 (dt, *J* = 15.4, 7.6 Hz, 1 H), 5.75 (dd, *J* = 15.4, 6.3 Hz, 1 H), 6.49 (d, *J* = 8.9 Hz, 2 H), 6.67 (d, *J* = 8.9 Hz, 2 H), 7.19 – 7.39 (m, 7 H), 7.62 (d, *J* = 8.3 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.8, 20.1, 21.5, 25.4, 40.0, 42.0, 47.0, 51.5, 55.7, 58.1, 114.5, 114.6, 125.7, 126.3, 126.6, 126.8, 126.9, 128.3, 129.4, 133.2, 133.8, 141.7, 143.2, 143.9, 151.7; HRMS calcd for $C_{32}H_{38}N_2O_3S$: 530.2603. Found *m/z* (relative intensity) 531 (M^++1, 37), 530.2604 (M^+, 100), 529 (4).

(2*S,4'*R**)-4,4-Dimethoxycarbonyl-2-[4-(*p*-anisidyl)-4-(*p*-anisyl)-(1*E*)-butenyl]-1-isopropylidenecyclopentane (2i)**: IR (neat) 3402 (m), 2947 (m), 1736 (s), 1512 (s), 1443 (m), 1242 (s), 1034 (m), 972 (w), 818 (w) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.54 (s, 3 H), 1.64 (s, 3 H), 2.10 (dm, *J* = 13.2 Hz, 1 H), 2.36 (dt, *J* = 14.2, 7.6 Hz, 1 H), 2.47 (ddd, *J* = 5.4, 6.6, 14.2 Hz, 1 H), 2.57 (dd, *J* = 8.5, 13.2 Hz, 1 H), 2.87 (br d, *J* = 16.3 Hz, 1 H), 2.95 (br d, *J* = 16.3 Hz, 1 H), 3.32 (br dd, *J* = 7.1, 8.5 Hz, 1 H), 3.67 (s, 3 H), 3.69 (s, 6 H), 3.70 (m, 1 H),

3.76 (s, 3 H), 3.92 (br s, 1 H), 4.19 (dd, *J* = 5.4, 7.6 Hz, 1 H), 5.27 (dt, *J* = 15.4, 6.6 Hz, 1 H), 5.40 (dd, *J* = 7.1, 15.4 Hz, 1 H), 6.43 (d, *J* = 9.0 Hz, 2 H), 6.65 (d, *J* = 9.0 Hz, 2 H), 6.83 (d, *J* = 8.7 Hz, 2 H), 7.22 (d, *J* = 8.7 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.8, 21.5, 38.7, 41.1, 42.0, 44.1, 52.6, 52.7, 55.2, 55.7, 57.6, 59.1, 113.8, 114.5, 114.6, 125.6, 126.1, 127.2, 132.7, 135.8, 136.0, 141.8, 151.7, 158.3, 172.0, 172.1; HRMS calcd for $C_{30}H_{37}NO_6$: 507.2621. Found *m*/*z* (relative intensity) 508 (M^++1, 33), 507.2618 (M^+, 100), 506 (6).

(2*S,4'*R**)-4,4-Dimethoxycarbonyl-2-[4-(*p*-anisidyl)-4-(*p*-chlorophenyl)-(1*E*)-butenyl]-1-isopropylidenecyclopentane** (**2j**): IR (neat) 3398 (w), 2910 (w), 1732 (s), 1514 (s), 1435 (s), 1242 (s), 1204 (s), 1090 (m), 1040 (w), 820 (s), 737 (w) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.53 (s, 3 H), 1.64 (s, 3 H), 2.10 (dd, *J* = 5.7, 13.2 Hz, 1 H), 2.35 (dt, *J* = 14.3, 7.7 Hz, 1 H), 2.49 (dt, *J* = 14.3, 5.7 Hz, 1 H), 2.57 (dd, *J* = 8.4, 13.2 Hz, 1 H), 2.87 (br d, *J* = 16.3 Hz, 1 H), 2.95 (br d, *J* = 16.3 Hz, 1 H), 3.32 (br dd, *J* = 7.0, 8.4 Hz, 1 H), 3.68 (s, 3 H), 3.70 (s, 3 H), 3.71 (s, 3 H), 4.22 (dd, *J* = 5.7, 7.7 Hz, 1 H), 5.25 (dt, *J* = 15.4, 7.7 Hz, 1 H), 5.42 (dd, *J* = 7.0, 15.4 Hz, 1 H), 6.41 (d, *J* = 8.8 Hz, 2 H), 6.67 (d, *J* = 8.8 Hz, 2 H), 7.26 (br s, 4 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.9, 21.5, 38.7, 41.1, 41.8, 44.1, 52.7, 55.7, 59.2, 114.8, 125.1, 126.4, 127.9, 128.7, 132.5, 132.6, 136.8, 141.4, 142.5, 152.3, 172.3, 172.4; HRMS calcd for $C_{29}H_{34}ClNO_5$: 511.2126. Found *m*/*z* (relative intensity) 511.2098 (M^+, 100).

(2*S,4'*R**)-4,4-Dimethoxycarbonyl-2-[4-(*p*-anisidyl)-4-(2-furfuryl)-(1*E*)-butenyl]-1-isopropylidenecyclopentane** (**2k**): IR (neat) 3398 (w), 2910 (w), 1732 (s), 1514 (s), 1435 (m), 1242 (s), 1204 (m), 1177 (m), 1040 (m), 822 (m), 739 (m) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.53 (s), 1.64 (s, 3 H), 2.07 (dd, *J* = 5.8, 13.4 Hz, 1 H), 2.53 – 2.59 (m, 3 H), 2.87 (br d, *J* = 16.5 Hz, 1 H), 2.93 (br d, *J* = 16.5 Hz, 1 H), 3.30 (br dd, *J* = 5.8, 7.0 Hz, 1 H), 3.70 (br s, 6 H), 3.72 (s, 3 H), 4.40 (t, *J* = 6.2 Hz, 1 H), 5.26 (dt, *J* = 15.6, 6.2 Hz, 1 H), 5.39 (dd, *J* = 7.0, 15.6 Hz, 1 H), 6.10 (d, *J* = 3.3 Hz, 1 H), 6.26 (br d, *J* = 3.3 Hz, 1 H), 6.57 (d, *J* = 8.8 Hz, 2 H), 6.72

(d, J = 8.8 Hz, 2 H), 7.32 (br s, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.8, 21.6, 37.8, 38.7, 41.1, 44.1, 52.7, 52.9, 55.7, 59.2, 106.2, 110.1, 114.8, 115.3, 124.9, 126.3, 132.9, 136.5, 141.2, 141.4, 152.6, 156.1, 172.3; HRMS calcd for $C_{27}H_{33}NO_6$: 467.2308. Found m/z (relative intensity) 468 (M^++1, 32), 467.2306 (M^+, 100).

(2*S,4'*R**)-4,4-Dimethoxycarbonyl-2-[4-(*p*-anisidyl)-6-phenyl-(1*E*)-hexenyl]-1-isopropylidenecyclopentane** (**2*l***): IR (neat) 3395 (m), 2497 (s), 2361 (s), 1736 (s), 1512 (s), 1442 (s), 1242 (s), 1065 (m), 818 (m), 748 (w), 702 (m) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.58 (s, 3 H), 1.66 (s, 3 H), 1.72 (dm, J = 5.7 Hz, 1 H), 1.82 (dm, J = 5.7 Hz, 1 H), 2.07 (dm, J = 13.2 Hz, 1 H), 2.23 (t, J = 5.7 Hz, 2 H), 2.58 (dm, J = 13.2 Hz, 1 H), 2.69 – 2.75 (m, 2 H), 2.91 (br s, 2 H), 3.24 – 3.36 (m, 2 H), 3.69 (s, 3 H), 3.72 (s, 3 H), 3.75 (s, 3 H), 5.30 (dm, J = 15.2 Hz, 1 H), 5.36 (dm, J = 15.2 Hz, 1 H), 6.51 (br d, J = 8.8 Hz, 2 H), 6.75 (d, J = 8.8 Hz, 2 H), 7.16 (d, J = 7.3 Hz, 2 H), 7.18 (t, J = 7.3 Hz, 1 H), 7.27 (t, J = 7.3 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.8, 21.6, 32.4, 36.0, 38.6, 41.1, 44.2, 52.6, 55.8, 59.1, 60.3, 114.9, 125.1, 125.7, 125.9, 128.2, 128.3, 132.9, 135.8, 141.9, 170.9, 172.1; HRMS calcd for $C_{31}H_{39}NO_5$: 505.2828. Found m/z (relative intensity) 506 (M^++1, 33), 505.2827 (M^+, 100).

(2*S,4'*R**)-4,4-Dimethoxycarbonyl-2-[4-(*p*-anisidyl)-4-cyclohexyl-(1*E*)-butenyl]-1-isopropylidenecyclopentane** (**2m**): IR (neat) 3402 (w), 2924 (s), 1736 (s), 1512 (s), 1443 (m), 1242 (s), 1042 (m), 818 (w) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.88 – 1.28 (m, 5 H), 1.43 (m, 1 H), 1.54 (s, 3 H), 1.64 (s, 3 H), 1.65 – 1.82 (m, 5 H), 2.02 (dd, J = 6.6, 13.2 Hz, 1H), 2.11 (dt, J = 13.9, 6.2 Hz, 1 H), 2.22 (dt, J = 13.9, 6.2 Hz, 1 H), 2.54 (dd, J = 8.5, 13.2 Hz, 1 H), 2.88 (br s, 2 H), 3.06 (dt, J = 8.5, 6.6 Hz, 1 H), 3.22 (m, 1 H), 3.28 (br t, J = 6.2 Hz, 1 H), 3.69 (s, 3 H), 3.70 (s, 3 H), 3.72 (s, 3 H), 5.26 (dd, J = 6.6, 15.4 Hz, 1 H), 5.33 (dt, J = 15.4, 6.2 Hz, 1 H), 6.50 (d, J = 8.8 Hz, 2 H), 6.73 (d, J = 8.8 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.7, 21.6, 26.5, 26.6, 29.1, 29.7, 34.5, 38.7, 41.2, 41.4, 44.2, 52.5, 52.6, 55.8, 58.9,

59.1, 114.3, 114.8, 125.9, 126.3, 132.9, 135.1, 142.8, 151.4, 172.1; HRMS calcd for $C_{29}H_{41}NO_5$: 483.2985. Found *m/z* (relative intensity) 483.2982 (M^+, 100), 482 (9), 424 (7).

(2*S,4*R**)-4,4-Dimethoxycarbonyl-2-[4-benzylamino-6-phenyl-(1*E*)-hexenyl]-1-isopropylidenecyclopentane (2n)**: IR (neat) 3449 (s), 2955 (s), 1736 (s), 1582 (s), 1497 (m), 1450 (s), 1373 (m), 1265 (s), 1204 (s), 1065 (s), 972 (s), 748 (s), 702 (s) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.50 (br s, 1 H), 1.55 (s, 3 H), 1.64 (s, 3 H), 1.73 (br dt, *J* = 14.2, 5.6 Hz, 2 H), 2.04 (dd, *J* = 6.2, 13.4 Hz, 1 H), 2.14 (dt, *J* = 13.1, 7.3 Hz, 1 H), 2.23 (dt, *J* = 13.9, 5.1 Hz, 1 H), 2.58 (dd, *J* = 8.5, 13.4 Hz, 1 H), 2.66 (t, *J* = 7.6 Hz, 1 H), 2.87 (br d, *J* = 16.0 Hz, 1 H), 2.93 (br d, *J* = 16.0 Hz, 1 H), 3.31 (m, 1 H), 3.67 (s, 3 H), 3.70 (s, 3 H), 3.74 (s, 2 H), 3.74 (m, 1 H), 5.33 (m, 2 H), 7.12- 7.33 (m, 10 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.7, 21.6, 32.0, 35.8, 36.8, 38.7, 41.2, 44.2, 51.2, 52.5, 52.6, 56.1, 59.1, 125.5, 126.0, 126.1, 126.7, 128.0, 128.2, 132.9, 135.3, 140.7, 142.5, 172.0, 172.1; HRMS calcd for $C_{31}H_{39}NO_4$: 489.2879. Found *m/z* (relative intensity) 490 (M^++1, 32), 489.2855 (M^+, 91), 488 (100), 459 (87).

(2*S,4*R**)-4,4-Dimethoxycarbonyl-2-[4-phenylamino-4-(2-furfuryl)-(1*E*)-butenyl]-1-isopropylidenecyclopentane (2o)**: IR (neat) 3395 (w), 1736 (s), 1605 (m), 1504 (s), 1435 (m), 1265 (s), 1204 (m), 1065 (s), 748 (m) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.46 (s, 3 H), 1.56 (s, 3 H), 2.01 (dd, *J* = 5.9, 13.2, Hz, 1 H), 2.48 (dd, *J* = 8.3, 13.2 Hz, 1 H), 2.49 (t, *J* = 5.9 Hz, 2 H), 2.80 (br d, *J* = 16.1 Hz, 1 H), 2.86 (br d, *J* = 16.1 Hz, 1 H), 3.23 (m, 1 H), 3.63 (s, 6 H), 3.69 (m, 1 H), 4.42 (t, *J* = 5.9 Hz, 1 H), 5.19 (dt, *J* = 15.3, 6.6, 1 H), 5.32 (dd, *J* = 7.1, 15.3 Hz, 1 H), 6.02 (d, *J* = 3.2 Hz, 1 H), 6.18 (dd, *J* = 1.7, 3.2 Hz, 1 H), 6.51 (d, *J* = 8.5 Hz, 2 H), 6.60 (t, *J* = 7.3 Hz, 1 H), 7.04 (dd, *J* = 7.3, 8.5 Hz, 1 H), 7.24 (br s, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.8, 21.5, 37.7, 38.6, 41.0, 44.1, 51.6, 52.6, 105.9, 110.0, 113.3, 117.5, 124.7, 129.0, 132.6, 136.3, 141.2, 147.0, 155.8, 172.1; HRMS calcd for $C_{26}H_{31}NO_5$: 437.2202. Found *m/z* (relative intensity) 438 (M^++1, 32), 437.2190 (M^+, 100), 406 (10), 345 (4).

(2*S,4*R**)-4,4-Dimethoxycarbonyl-2-[4-(*p*-chlorophenylamino)-4-(2-furfuryl)-(1*E*)-butenyl]-1-isopropylidenecyclopentane (2q)**: IR (neat) 3395 (m), 2916 (s), 1736 (s), 1597 (m), 1504 (s), 1435 (m), 1065 (m), 972 (w), 818 (m), 741 (m), 671 (w) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.52 (s, 3 H), 1.63 (s, 3 H), 2.10 (dd, *J* = 5.6, 13.2 Hz, 1 H), 2.52 – 2.57 (m, 3 H), 2.87 (d, *J* = 16.1 Hz, 1 H), 2.91 (d, *J* = 16.1 Hz, 1 H), 3.30 (m, 1 H), 3.70 (br s, 6 H), 4.44 (t, *J* = 6.0 Hz, 1 H), 5.24 (dt, *J* =7.1, 14.1 Hz, 1 H), 5.40 (dd, *J* = 7.1, 15.2 Hz, 1 H), 6.07 (d, *J* = 3.2 Hz, 1 H), 6.26 (dd, *J* = 1.7, 3.2 Hz, 1 H), 6.51 (d, *J* = 8.9 Hz, 2 H), 7.05 (d, *J* = 8.9 Hz, 2 H), 7.31 (br s, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.8, 21.5, 37.6, 37.8, 40.9, 44.1, 51.6, 52.6, 59.1, 60.3, 106.1, 110.0, 114.1, 122.1, 124.4, 126.1, 128.8, 12.6, 136.4, 141.3, 145.6, 155.3, 172.1, 172.2; HRMS calcd for $C_{26}H_{30}ClNO_5$: 471.1813. Found *m*/*z* (relative intensity) 472 (M^++1, 31), 471.1797 (M^+, 100).

(2*S,4*R**)-4,4-Dimethoxycarbonyl-2-[4-benzylamino-4-(2-furfuryl)-(1*E*)-butenyl]-1-isopropylidenecyclopentane (2s)**: IR (neat) 3340 (w), 2947 (w), 1736 (s), 1450 (m), 1258 (s), 1204 (s), 1065 (m), 741 (s) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.47 (s, 3 H), 1.86 (m, 1 H), 2.01 (dd, *J* = 6.1, 13.2 Hz, 1 H), 2.43 (m, 2 H), 2.57 (dd, *J* = 8.4, 13.2 Hz, 1 H), 2.84 (d, *J* = 15.9 Hz, 1 H), 2.90 (d, *J* = 15.9 Hz, 1 H), 3.26 (m, 1 H), 3.58 (d, *J* = 13.1 Hz, 1 H), 3.67 (s, 3 H), 3.70 (s, 3 H), 3.71 (m, 1 H), 3.74 (d, *J* = 13.1 Hz, 1 H), 5.25 (dt, *J* = 15.3, 6.2 Hz, 1 H), 5.31 (dd, *J* = 6.3, 15.3 Hz, 1 H), 6.14 (d, *J* = 2.9 Hz, 1 H), 6.30 (dd, *J* = 1.8, 2.9 Hz, 1 H), 7.20 – 7.31 (m, 5 H), 7.35 (br s, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.7, 21.6, 37.9, 38.7, 41.1, 44.0, 51.2, 52.5, 52.6, 55.3, 59.1, 106.4, 109.7, 125.7, 126.0, 126.7, 128.1, 128.2, 132.6, 135.4, 140.1, 141.3, 156.2, 172.0, 172.1; HRMS calcd for $C_{27}H_{33}NO_5$: 451.2359. Found *m*/*z* (relative intensity) 452 (M^++1, 34), 451.2350 (M^+, 70), 420 (100), 392 (3), 384 (19).

(2*S,4*R**)-4,4-Dimethoxycarbonyl-2-[4-(*p*-anisidyl)-4-phenyl-(1*E*)-butenyl]-(1*Z*)-1-(2-**

butylidene)cyclopentane (3a): IR (neat) 3395 (w), 2955 (m), 1736 (s), 1512 (s), 1450 (m), 1242 (s), 1034 (m), 972 (w), 818 (m), 756 (w), 702 (w) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.83 (t, *J* = 7.3 Hz, 3 H), 1.61 (s, 3 H), 1.91 (dq, *J* = 14.9, 7.3 Hz, 1 H), 1.95 (dq, *J* = 14.9, 7.3 Hz, 1 H), 2.12 (dd, *J* = 5.4, 13.2 Hz, 1 H), 2.36 (dt, *J* = 14.4, 7.8 Hz, 1 H), 2.51 (dt, *J* = 14.4, 5.4 Hz, 1 H), 2.54 (dd, *J* = 8.3, 13.2 Hz, 1 H), 2.84 (br d, *J* = 16.5 Hz, 1 H), 2.96 (br d, *J* = 16.5 Hz, 1 H), 3.35 (m, 1 H), 3.66 (s, 3 H), 3.71 (s, 6 H), 4.23 (dd, *J* = 5.4, 7.8 Hz, 1 H), 5.30 (dt, *J* = 15.1, 7.8 Hz, 1 H), 5.44 (dd, *J* = 7.1, 15.1 Hz, 1 H), 6.44 (d, *J* = 9.0 Hz, 2 H), 6.65 (d, *J* = 9.0 Hz, 2 H), 7.16-7.34 (m, 5 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 12.3, 18.3, 27.4, 30.8, 38.6, 41.1, 41.9, 43.7, 52.6, 55.7, 58.2, 59.0, 114.5, 114.6, 125.5, 126.2, 126.7, 128.3, 131.8, 132.1, 136.6, 141.7, 143.9, 151.8, 172.1, 172.2; HRMS calcd for $C_{30}H_{37}NO_5$: 491.2672. Found *m*/*z* (relative intensity) 492 (M^++1, 36), 491.2671 (M^+, 100), 490 (4), 460 (8), 460 (8).

(2*S,4*R**)-4,4-Dimethoxycarbonyl-2-[4-(*p*-anisidyl)-4-phenyl-(1*E*)-butenyl]-(1*E*)-1-phenylethylidenecyclopentane (4)**: 3402 (w), 2951 (m), 1732 (s), 1514 (s), 1435 (m), 1240 (s), 1038 (m), 968 (w), 820 (m), 766 (m), 702 (s) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.57 (m, 1 H), 1.97 (s, 3 H), 2.06 (dt, *J* = 14.4, 7.8 Hz, 1 H), 2.11 (dd, *J* = 6.3, 13.2 Hz, 1 H), 2.18 (dt, *J* = 14.4, 4.4 Hz, 1 H), 2.49 (dd, *J* = 7.8, 13.2 Hz, 1 H), 3.06 (br d, *J* = 16.8 Hz, 1 H), 3.12 (br d, *J* = 16.8 Hz, 1 H), 3.34 (m, 1 H), 3.68 (s, 3 H), 3.73 (s, 3 H), 3.76 (s, 3 H), 4.04 (dd, *J* = 4.4, 7.8 Hz, 1 H), 4.90 (br dt, *J* = 15.1, 7.8 Hz, 1 H), 5.10 (dd, *J* = 7.3, 15.1 Hz, 1 H), 6.40 (d, *J* = 9.0 Hz, 2 H), 6.65 (d, *J* = 9.0 Hz, 2 H), 7.00-7.32 (m, 10 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.1, 38.9, 41.1, 41.9, 44.6, 52.7, 52.8, 55.7, 58.0, 58.7, 114.6, 126.1, 126.2, 126.6, 127.7, 128.3, 131.4, 134.9, 136.2, 141.6, 143.3, 144.0, 151.8, 172.1; HRMS calcd for $C_{34}H_{37}NO_5$: 539.2672. Found *m*/*z* (relative intensity) 540 (M^++1, 39), 539.2670 (M^+, 100), 538 (4), 508 (10).

(2*S,4*R**)-4,4-Dimethoxycarbonyl-2-[4-(*p*-anisidyl)-4-phenyl-(1*E*)-butenyl]-(1*Z*)-1-(1-**

trimethylsilyl-2-propylidene)cyclopentane (5): IR (neat) 3402 (m), 2955 (s), 1736 (s), 1512 (s), 1450 (s), 1242 (s), 1173 (s), 1042 (s), 972 (s) , 849 (s), 756 (s), 702 (s) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.33 (s, 9 H), 1.30 (d, *J* = 13.4 Hz, 1 H), 1.69 (s, 3 H), 1.83 (d, *J* = 13.4 Hz, 1 H), 2.12 (dd, *J* = 6.0, 13.4 Hz, 1 H), 2.44 (dt, *J* = 13.9, 7.3 Hz, 1 H), 2.60 (dt, *J* = 13.9, 5.0 Hz, 1 H), 2.64 (dd, *J* = 8.5, 13.4 Hz, 1 H), 2.98 (br s, 2 H), 3.26 (m, 1 H), 3.74 (s, 3 H), 3.76 (s, 3 H), 3.78 (s, 3 H), 4.31 (dd, *J* = 5.0, 7.3 Hz, 1 H), 5.36 (dt, *J* = 15.1, 7.3 Hz, 1 H), 5.45 (dd, *J* = 7.3, 15.1 Hz, 1 H), 6.49 (d, *J* = 8.9 Hz, 2 H), 6.72 (d, *J* = 8.9 Hz, 2 H), 7.20-7.40 (m, 5 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ -0.5, 22.1, 25.4, 38.8, 41.3, 41.9, 44.2, 52.6, 55.7, 58.2, 59.2, 114.6, 125.4, 126.2, 126.7, 128.4, 128.5, 129.7, 136.6, 141.6, 143.8, 151.8, 172.0, 172.2; HRMS calcd for $C_{32}H_{43}NO_5Si$: 549.2911. Found *m/z* (relative intensity) 550 (M^++1, 38), 549.2906 (M^+, 100), 548 (5), 534 (10), 518 (9).

3-Ispropylidene-4-[4-(*p*-anisidyl)-8-hydroxy-(1*E*)-octenyl]tetrahydrofuran (7b): IR (neat) 3379 (s), 2932 (s), 1512 (s), 1450 (w), 1234 (s), 1049 (s), 818 (w) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.36-1.61 (m, 6 H), 1.59 (s, 3 H), 1.65 (s, 3 H), 2.22 (t, *J* = 5.6 Hz, 2 H), 3.28 (m, 2 H), 3.61 (t, *J* = 6.1 Hz, 2 H), 3.69 (dd, *J* = 2.7, 8.5 Hz, 1 H), 3.73 (s, 3 H), 3.85 (dd, *J* = 6.1, 8.5 Hz, 1 H), 4.24 (brd, *J* = 12.7 Hz, 1 H), 4.32 (brd, *J* = 12.7 Hz, 1 H), 5.40 (dt, *J* = 15.4 Hz, 5.7 Hz, 1 H, coalescing to d, J = 13.9 Hz by irradiation at 2.22), 5.44 (dd, *J* = 15.4, 10.9 Hz, 1 H), 6.51 (d, *J* = 8.9 Hz, 2 H), 6.74 (d, *J* = 8.9 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.0, 21.1, 22.2, 32.7, 34.2, 37.1, 45.7, 53.8, 55.8, 62.6, 70.1, 74.7, 114.7, 114.9, 123.3, 125.9, 133.5, 133.9, 141.8, 151.7; HRMS calcd for $C_{22}H_{33}NO_3$: 359.2460, found *m/z* (relative intensity) 360 (M^++1, 36), 359.2445 (M^+, 100), 345 (2), 342 (4), 341 (11).

3-[(1*Z*)-Phenylethylidene]-4-[4-(*p*-anisidyl)-8-hydroxy-(1*E*)-octenyl]tetrahydrofuran (7c): IR (neat) 3379 (w), 2932 (m), 1512 (s), 1443 (w), 1234 (m), 1034 (m), 818 (w), 702 (s) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.41-1.73 (m, 6 H), 2.02 (s, 3 H), 2.27 (dd, *J* = 5.4, 13.4 Hz, 1

H), 2.32 (dd, *J* = 5.9, 13.4 Hz, 1 H), 3.34 (m, 1 H), 3.47 (m, 1 H), 3.63 (t, *J* = 6.2 Hz, 3 H), 3.70 (dd, *J* = 3.8 Hz, 1 H), 3.73 (s, 3 H), 3.97 (dd, *J* = 6.7, 8.7 Hz, 1 H), 4.12 (br d, *J* = 13.2 Hz, 1 H), 4.32 (br d, *J* = 12.9 Hz, 1 H), 5.51 (dd, *J* = 6.6, 15.4 Hz, 1 H), 5.56 (dt, *J* = 5.9, 15.4 Hz, 1 H), 6.55 (d, *J* = 8.8 Hz, 2 H), 6.75 (br d, *J* = 8.8 Hz, 2 H), 7.13 (br d, *J* = 7.1 Hz, 2 H), 7.27 (m, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.8, 22.2, 32.7, 46.3, 53.9, 55.8, 62.7, 70.5, 74.2, 114.9, 126.6, 126.8, 126.9, 128.1, 129.0, 132.8, 137.5, 143.1, 151.9; HRMS calcd for $C_{27}H_{35}NO_3$: 421.2617. Found *m*/*z* (relative intensity) 422 (M^++1, 40), 421.2605 (M^+, 100), 406 (1).

3-[(1*Z*)-Trimethylsilylethylidene]-4-[4-(*p*-anisidyl)-8-hydroxy-(1*E*)-octenyl]tetrahydrofuran (7d): IR (neat) 3373 (s), 2933 (s), 2858 (s), 1512 (s), 1248 (s), 1042 (m), 835 (m), 756 (w) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.10 (s, 9 H), 1.40-1.62 (m, 6 H), 1.70 (s, 3 H), 2.25 (t, *J* = 5.5 Hz, 2 H), 3.30 (m, 1 H), 3.42 (m, 1 H), 3.62 (t, *J* = 6.2 Hz, 2 H), 3.69 (dd, *J* = 2.7, 8.5 Hz, 1 H), 3.74 (s, 3 H), 3.83 (dd, *J* = 6.3, 8.5 Hz, 1 H), 4.22 (dd, *J* = 2.0, 13.1 Hz, 1 H), 4.33 (dt, *J* = 13.1, 2.0 Hz, 1 H), 5.38 (dd, *J* = 6.1, 15.6 Hz, 1 H), 5.42 (dt, *J* = 15.6, 7.2 Hz, 1 H), 6.59 (br d, *J* = 8.7 Hz, 2 H), 6.75 (d, *J* = 8.7 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 0.8, 18.8, 22.2, 32.7, 33.7, 36.6, 46.6, 55.8, 62.6, 70.8, 73.7, 114.9, 126.0, 126.4, 133.0, 150.1; HRMS calcd for $C_{24}H_{39}NO_3Si$: 417.2699. Found *m*/*z* (relative intensity) 418 (M^++1, 33), 417.2699 (M^+, 100), 416 (6), 402 (10).

3-Isopropylidene-4-[4-(*p*-anisidyl)-8-hydroxy-(1*E*)-octenyl]-*N*-(*p*-toluenesulfonyl)pyrrolidine (7e) : IR (neat) 3395 (m), 2932 (s), 1512 (s), 1450 (m), 1342 (s), 1234 (s), 1165 (s), 1096 (m), 1042 (s), 818 (s), 664 (s) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.43-1.61 (m, 6 H), 1.54 (s, 3 H), 1.56 (s, 3 H), 2.19 (t, *J* = 5.6 Hz, 2 H), 3.04 (dd, *J* = 6.5, 9.2 Hz, 1 H), 3.20-3.34 (m, 2 H), 3.29 (dd, *J* = 1.8, 9.2 Hz, 1 H), 3.53 (brd, *J* = 13.7 Hz, 1 H), 3.63 (t, *J* = 6.3 Hz, 2 H), 3.74 (s, 3 H), 3.90 (brd, *J* = 13.7 Hz, 1 H), 5.33 (dd, *J* = 5.6, 15.3 Hz, 1 H),

5.38 (dt, *J* = 15.3, 6.1 Hz, 1 H), 6.57 (d, *J* = 8.9 Hz, 2 H), 6.76 (d, *J* = 8.9 Hz, 2 H), 7.31 (d, *J* = 8.1 Hz, 2 H), 7.69 (d, *J* = 8.1 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.5, 21.1, 21.5, 22.1, 30.9, 32.6, 33.8, 36.7, 44.0, 50.3, 54.3, 55.8, 62.5, 114.9, 115.3, 126.1, 126.3, 127.8, 129.5, 129.9, 132.4, 132.7, 140.9, 143.4, 152.2; HRMS calcd for $C_{29}H_{40}N_2O_4S$: 512.2709. Found *m/z* (relative intensity) 513 (M^++1, 37), 512.2696 (M^+, 100), 511 (8), 495 (4), 494 (7).

4,4-Dimethoxycarbonyl-2-[4-(*p*-anisidyl)-8-hydroxy-(1*E*)-octenyl]-1-isopropylidenecyclohexane (7f): IR (neat) 3395 (w), 2932 (m), 1728 (s), 1512 (s), 1450 (m), 1242 (s), 1042 (m), 818 (w), 741 (w) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.36-1.62 (m, 6 H), 1.58 (s, 3 H), 1.65 (dd, *J* = 4.6, 12.9 Hz, 1 H), 1.69 (s, 3 H), 2.18 (m, 4 H), 2.37 (m, 2 H), 2.48 (br dt, *J* = 14.9, 3.9 Hz, 1 H), 3.26 (m, 1 H), 3.44 (m, 1 H), 3.63 (t, *J* = 6.5 Hz, 2 H), 3.68 (s, 6 H), 3.73 (s, 3 H), 5.21 (ddt, *J* = 1.7, 15.4, 7.3 Hz, 1 H), 5.37 (dd, *J* = 4.9, 15.4 Hz, 1 H), 6.57 (d, *J* = 8.8 Hz, 2 H), 6.75 (d, *J* = 8.8 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.8, 20.1, 22.3, 22.4, 31.3, 32.7, 34.1, 35.9, 37.3, 38.5, 52.3, 52.6, 53.8, 55.8, 62.7, 114.6, 114.9, 124.9, 125.5, 128.7, 134.4, 142.0, 151.7, 172.1, 172.6; HRMS calcd for $C_{28}H_{41}NO_6$: 487.2934. Found *m/z* (relative intensity) 488 (M^++1, 32), 487.2925 (M^+, 100), 414 (7).

4,4-Dimethoxycarbonyl-2-[4-(*p*-anisidyl)-8-hydroxy-(1*E*)-octenyl]-(1*Z*)-ethylidenecyclopentane (7i): IR (neat) 3395 (w), 2939 (m), 1736 (s), 1512 (s), 1435 (m), 1242 (s), 1041 (m), 818 (m), 733 (m) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.42-1.65 (m, 9 H), 1.95 (dd, *J* = 7.1, 13.4 Hz, 1 H), 2.16 (s, 3 H), 2.20 (t, *J* = 6.2 Hz, 2 H), 2.65 (dd, *J* = 8.5, 13.4 Hz, 1 H), 2.79 (br d, *J* = 15.6 Hz, 1 H), 2.96 (dq, *J* = 15.6, 2.4 Hz, 1 H), 3.25- 3.35 (m, 2 H), 3.62 (t, *J* = 6.3 Hz, 2 H), 3.70 (s, 6 H), 3.73 (s, 3 H), 5.26-5.50 (m, 3 H), 6.53 (d, *J* = 8.9 Hz, 2 H), 6.75 (d, *J* = 8.9 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.0, 22.1, 32.6, 33.9, 36.7, 41.0, 41.7, 42.5, 52.6, 53.6, 58.8, 62.6, 114.6, 114.8, 119.0, 125.6, 135.0, 140.3, 141.8, 151.7; HRMS calcd for $C_{26}H_{37}NO_6$: 459.2621. Found *m/z* (relative intensity) 460 (M^++1, 35),

459.2615 (M^+, 100), 458 (11).

4,4-Dimethoxycarbonyl-2-[4-(*p*-anisidyl)-7-hydroxy-(1*E*)-heptenyl]-1-isopropylidenecyclopentane (**7j**): IR (neat) 3383 (w), 2934 (w), 1732 (s), 1512 (s), 1435 (m), 1244 (m), 1040 (m), 822 (m) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.50 (m, 1 H), 1.57 (s, 3 H), 1.65 (s, 3 H), 1.61 – 1.75 (m, 3 H), 2.06 (dd, *J* = 6.0, 13.4 Hz, 1 H), 2.17 – 2.26 (m, 2 H), 2.57 (dd, *J* = 8.5, 13.4 Hz, 1 H), 2.90 (br s, 2 H), 3.24 – 3.34 (m, 2 H), 3.64 (dt, *J* = 5.6, 2.6 Hz, 2 H), 3.69 (s, 3 H), 3.70 (s, 3 H), 3.74 (s, 3 H), 5.28 (dd, *J* = 6.0, 15.2 Hz, 1 H), 5.33 (dt, *J* = 15.2, 5.9 Hz, 1 H), 6.64 (d, *J* = 8.9 Hz, 2 H), 6.76 (d, *J* = 8.9 Hz, 2 H); ^1H NMR (400 MHz, THF-d_8) δ 1.40 – 1.62 (m, 4 H), 1.59 (s, 3 H), 1.64 (s, 3 H), 2.01 (dd, *J* = 6.2, 13.1 Hz, 1 H), 2.17 (br dt, *J* = 13.8, 7.3 Hz, 1 H), 2.19 (br dt, *J* = 13.8, 7.3 Hz, 1 H), 2.58 (dm, *J* = 13.1 Hz, 1 H), 2.84 (br d, *J* = 16.3 Hz, 1 H), 2.90 (br d, *J* = 16.3 Hz, 1 H), 3.28 (br t, *J* = 7.3 Hz, 1 H), 3.32 (br d, *J* = 6.2 Hz, 1 H), 3.43 – 3.50 (m, 2 H), 3.63 (s, 3 H), 3.64 (s, 3 H), 3.65 (s, 3 H), 3.97 (m, 1 H), 5.30 (dd, *J* = 7.4, 15.2 Hz, 1 H), 5.43 (dt, *J* = 15.2, 7.3 Hz, 1 H), 6.50 (d, *J* = 9.0 Hz, 2 H), 6.58 (d, *J* = 9.0 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.8, 21.6, 29.6, 30.9, 31.1, 36.7, 38.6, 41.1, 44.2, 52.6, 55.2, 55.3, 59.1, 62.8, 114.9, 116.3, 124.9, 126.0, 132.8, 136.1, 140.2, 152.8, 172.1, 172.2; HRMS calcd for $C_{26}H_{37}NO_6$: 459.2621. Found *m/z* (relative intensity) 460 (M^++1, 29), 459.2605 (M^+, 100), 442 (28), 441 (29).

4,4-Dimethoxycarbonyl-2-[4-(*p*-anisidyl)-7-hydroxy-7-(β-naphthyl)-(1*E*)-heptenyl]-1-isopropylidenecyclopentane (7k): IR (neat) 3395 (s), 2947 (s), 1736 (s), 1512 (s), 1443 (s), 1242 (s), 1042 (s), 826 (s), 748 (s) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, major isomer) δ 1.48 (s, 3 H), 1.61 (s, 3 H), 1.72 (m, 2 H), 1.98 (m, 2 H), 2.05 (dd, *J* = 4.5, 13.2 Hz, 1 H), 2.18 (m, 2 H), 2.53 (dd, *J* = 8.2, 13.2 Hz, 1 H), 2.87 (br s, 2 H), 3.28 (m, 2 H), 3.67 (s, 3 H), 3.70 (s, 3 H), 3.73 (s, 3 H), 4.88 (t, *J* = 5.9 Hz, 1 H), 6.60 (d, *J* = 8.8 Hz, 2 H), 6.73 (d, *J* = 7.1 Hz, 2 H), 7.45 (m, 3 H), 7.80 (m, 4 H); ^1H NMR (400 MHz, $CDCl_3$, minor isomer) δ 1.49 (s, 3 H), 1.61 (s, 3

H), 3.67 (s, 3 H), 3.70 (s, 3 H), 3.74 (s, 3 H), 4.85 (t, *J* = 5.9 Hz, 2 H), 6.64 (d, *J* = 8.8 Hz, 2 H), 6.75 (d, *J* = 7.1 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$, a mixture of 2 isomers) δ 20.8, 21.6, 30.2, 30.9, 35.6, 36.3, 36.8, 38.8, 41.1, 44.1, 44.2, 52.7, 55.8, 59.2, 74.3, 74.7, 114.9, 116.2, 116.5, 124.0, 124.4, 124.9, 125.7, 126.0, 127.6, 127.9, 128.2, 132.8, 136.1, 136.2, 142.0, 153.0, 172.2; HRMS calcd for $C_{36}H_{43}NO_6$: 585.3090. Found *m/z* (relative intensity) 586 (M^++1, 39), 585.3088 (M^+, 100), 584 (3), 568 (10), 567 (23).

4,4-Dimethoxycarbonyl-2-[4-(*p*-anisidyl)-6,6-dimethyl-8-hydroxy-(1*E*)-octenyl]-1-isopropylidenecyclopentane (7*l*): IR (neat) 3549 (m), 3371 (s), 2955 (s), 1736 (s), 1512 (s), 1443 (s), 1242 (s), 1042 (s), 972 (m), 818 (s), 756 (w) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.94 (s, 3 H), 0.95 (s, 3 H), 1.42 (dd, *J* = 7.3, 14.6 Hz, 1 H), 1.49 (dt, *J* = 7.3, 14.6 Hz, 1 H), 1.56 (m, 1 H), 1.59 (s, 3 H), 1.65 (s, 3 H), 1.67 (dt, *J* = 14.6, 7.3 Hz, 1 H), 2.02 (dd, *J* = 13.2, 6.3 Hz, 1 H), 2.12 (dt, *J* = 13.4, 6.8 Hz, 1 H), 2.23 (dt, *J* = 13.4, 4.6 Hz, 1 H), 2.58 (dd, *J* = 8.5, 13.2 Hz, 1 H), 2.89 (br s, 2 H), 3.33 (m, 2 H), 3.69 (m, 2 H), 3.70 (s, 3 H), 3.71 (s, 3 H), 3.71 (t, *J* = 7.3 Hz, 2 H), 3.74 (s, 3 H), 5.31 (m, 2 H), 6.62 (d, *J* = 9.0 Hz, 2 H), 6.77 (d, *J* = 9.0 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.9, 21.6, 28.4, 28.7, 32.6, 38.7, 41.3, 44.2, 46.1, 46.2, 51.9, 52.7, 55.8, 59.2, 59.6, 115.0, 115.8, 125.2, 126.0, 133.0, 136.2, 140.1, 152.6, 172.2; HRMS calcd for $C_{29}H_{43}NO_6$: 501.3090. Found *m/z* (relative intensity) 502 (M^++1, 34), 501.3089 (M^+, 100), 500 (12), 484 (5), 483 (13), 470 (16).

4,4-Dimethoxycarbonyl-2-[4-(*p*-anisidyl)-8-hydroxy-(1*E*,9)-decadienyl]-1-isopropylidenecyclopentane (7m): (a mixture of 2 isomers in 4 : 1 ratio): IR (neat) 3395 (m), 2932 (s), 1736 (s), 1510 (s), 1435 (s), 1242 (s), 1042 (s), 818 (m), 733 (m) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, a major isomer was assigned) δ 1.38-1.68 (m, 6 H), 1.57 (s, 3 H), 1.65 (s, 3 H), 2.06 (dd, *J* = 6.0, 13.3 Hz, 1 H), 2.19 (t, *J* = 5.6 Hz, 2 H), 2.57 (dd, *J* = 8.4, 13.3 Hz, 1 H), 2.90 (br s, 2 H), 3.27 (m, 1 H), 3.31 (m, 1 H), 3.69 (s, 3 H), 3.71 (s, 3 H), 3.74 (s, 3 H), 4.09 (q, *J* =

5.6 Hz, 1 H), 5.09 (dm, *J* = 10.6 Hz, 1 H), 5.20 (dm, *J* = 17.1 Hz, 1 H), 5.32 (m, 2 H), 5.85 (ddd, *J* = 5.6, 10.6, 17.1 Hz, 1 H), 6.53 (d, *J* = 8.9 Hz, 2 H), 6.75 (d, *J* = 8.9 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$, a major isomer was assigned) δ 20.8, 21.6, 21.8, 34.1, 36.8, 37.0, 38.7, 41.2, 44.2, 52.6, 53.8, 53.9, 55.8, 59.1, 72.9, 114.5, 114.9, 125.3, 125.9, 132.9, 135.7, 141.0, 151.8, 172.1, 172.2; ^{13}C NMR (100 MHz, $CDCl_3$, a minor isomer was assigned) δ 14.2, 24.0, 24.7, 27.1, 30.7, 34.7, 34.9, 36.3, 37.0, 47.9, 55.6, 55.7, 55.9, 69.1, 70.5, 115.2, 116.6, 119.7, 121.6, 137.0, 139.2, 139.4, 141.7, 152.0; HRMS calcd for $C_{29}H_{41}NO_6$: 499.2934. Found *m/z* (relative intensity) 500 (M^++1, 34), 499.2931 (M^+, 100), 468 (12).

4,4-Dimethoxycarbonyl-2-[4-(*p*-anisidyl)-6-(*o*-hydroxyphenyl)-(1*E*)-hexenyl]-1-isopropylidenecyclopentane (7n) : IR (neat) 3402 (w), 2947 (m), 1736 (s), 1589 (w), 1512 (s), 1450 (s), 1242 (s), 1042 (m), 826 (w), 756 (m) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.54 (s, 3 H), 1.66 (s, 3 H), 1.70 (m, 1 H), 1.91 (m, 1 H), 2.05 (dd, *J* = 5.9, 13.2 Hz, 1 H), 2.09 (m, 2 H), 2.54 (dd, *J* = 8.4, 13.2 Hz, 1 H), 2.67 (dt, *J* = 13.7, 4.4 Hz, 1 H), 2.90 (br s, 2 H), 2.93 (dt, *J* = 13.7, 5.6 Hz, 1 H), 3.19 (br dq, *J* = 10.3, 4.4 Hz, 1 H), 3.27 (m, 1 H), 3.67 (s, 3 H), 3.75 (s, 3 H), 5.19 (m, 2 H), 6.68 (d, *J* = 9.0 Hz, 2 H), 6.78 (d, *J* = 9.0 Hz, 2 H), 6.85 (d, *J* = 9.3 Hz, 2 H), 7.07 (dt, *J* = 1.5, 7.8 Hz, 1 H), 7.10 (dt, *J* = 1.7, 7.8 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.8, 21.5, 26.4, 34.9, 35.9, 38.6, 40.9, 44.1, 52.6, 52.7, 53.4, 55.6, 59.1, 114.8, 116.5, 118.3, 120.1, 124.0, 125.9, 127.4, 130.1, 132.8, 136.3, 139.5, 153.8, 155.3, 172.1, 172.3; HRMS calcd for $C_{31}H_{39}NO_6$: 521.2777. Found *m/z* (relative intensity) 522 (M^++1, 36), 521.2765 (M^+, 100), 520 (7), 490 (7), 462 (5).

4,4-Dimethoxycarbonyl-2-[4-(*p*-anisidyl)-4-(5-hydroxymethyl-2,2-dimethyl-1,3-dioxolan-4-yl)-(1*E*)-butenyl]-1-isopropylidenecyclopentane (7p): IR (neat) 3356 (s), 2986 (s), 2947 (s), 1728 (s), 1512 (s), 1450 (s), 1373 (s), 972 (s), 826 (s), 749 (s) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.37 (s, 3 H), 1.46 (s, 3 H), 1.62 (s, 3 H), 2.11 (dd, *J* = 5.2, 13.4

Hz, 1 H), 2.31 (m, 2 H), 2.53 (dd, *J* = 8.7, 13.4 Hz, 1 H), 2.89 (dd, *J* = 1.7, 16.3 Hz, 1 H), 2.98 (d, *J* = 16.3 Hz, 1 H), 3.35 (m, 1 H), 3.65 (m, 1 H), 3.70 (s, 3 H), 3.71 (t, *J* = 7.3 Hz, 2 H), 3.72 (s, 3 H), 3.75 (s, 3 H), 3.96 (dd, *J* = 5.6, 10.1 Hz, 1 H), 4.35 (dt, *J* = 5.6, 7.3 Hz, 1 H), 5.29 (dd, *J* = 5.8, 15.4 Hz, 1 H), 5,35 (dt, *J* = 7.3, 15.4 Hz, 1 H), 6.68 (d, *J* = 9.0 Hz, 2 H), 6.79 (d, *J* = 9.0 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.0, 21.5, 25.2, 27.9, 32.2, 38.5, 40.8, 44.3, 52.8, 53.6, 55.7, 59.2, 61.0, 76.6, 77.9, 108.2, 115.0, 117.6, 122.9, 125.8, 133.0, 137.8, 139.2, 153.6, 172.4; HRMS calcd for $C_{29}H_{41}NO_5$: 531.2832. Found *m/z* (relative intensity) 532 (M^++1, 35), 531.2833 (M^+, 100), 530 (2), 516 (19), 500 (8).

4,4-Dimethoxycarbonyl-2-[4-phenylamino-8-hydroxy-(1*E*)-octenyl]-1-isopropylidenecyclopentane (7q): IR (neat) 3400 (w), 2932 (m), 1732 (s), 1601 (s), 1504 (m), 1435 (m), 1267 (s), 1204 (m), 1065 (m), 752 (s), 694 (m) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.30-1.55 (m, 6 H), 1.50 (s, 3 H), 1.58 (s, 3 H), 1.98 (dd, *J* = 6.1 Hz, 1 H), 2.14 (t, *J* = 5.9 Hz, 2 H), 2.50 (dd *J* = 8.4, 13.2 Hz, 1 H), 2.83 (br s, 2 H), 3.24 (m, 1 H), 3.30 (t, *J* = 5.9 Hz, 1 H), 3.56 (t, *J* = 6.3 Hz, 2 H), 3.63 (s, 3 H), 3.64 (s, 3 H), 5.23 (dd, *J* = 4.9, 15.1 Hz, 1 H), 5.28 (dt, *J* = 6.1, 15.1 Hz, 1 H), 6.48 (d, *J* = 8.5 Hz, 2 H), 6.57 (t, *J* = 7.3 Hz, 1 H), 7.06 (dd, *J* = 7.3, 8.5 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.8, 21.6, 22.3, 30.9, 32.7, 34.1, 37.0, 38.7, 41.2, 44.2, 52.6, 52.7, 59.1, 62.7, 113.1, 116.8, 125.3, 126.0, 129.1, 132.9, 135.7, 147.6, 172.1, 172.2; HRMS calcd for $C_{26}H_{37}NO_5$: 443.2672. Found *m/z* (relative intensity) 444 (M^++1, 67), 443.2673 (M^+, 100), 442 (10), 412 (37), 370 (24).

4,4-Dimethoxycarbonyl-2-[4-(*o*-anisidyl)-8-hydroxy-(1*E*)-octenyl]-1-isopropylidenecyclopentane (7r): IR (neat) 3418 (br), 2862 (m), 1736 (s), 802 (s) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.35-1.62 (m, 6 H), 1.56 (s, 3 H), 1.64 (s, 3 H), 2.01 (dd, *J* = 6.5, 13.2 Hz, 1 H), 2.22 (t, *J* = 6.1 Hz, 2 H), 2.58 (dd, *J* = 8.3, 13.2 Hz, 1 H), 2.88 (s, 2 H), 3.28 (m, 1 H), 3.35 (quint, *J* = 6.1 Hz, 1 H, coalsing to t, *J* = 6.1 Hz by irradiation at 2.22), 3.62 (t, *J* =

6.3 Hz, 2 H), 3.69 (s, 3 H), 3.70 (s, 3 H), 3.82 (s, 3 H), 5.30 (dd, *J* = 6.1, 15.4 Hz, 1 H), 5.37 (dt, *J* = 15.4, 6.1 Hz, 1 H, coalescing to d, *J* = 15.1 Hz by irradiation at 2.22), 6.56 (dd, *J* = 1.2, 7.8 Hz, 1 H), 6.60 (dt, *J* = 1.2, 7.8 Hz, 1 H), 6.74 (dd, *J* = 1.2, 7.9 Hz, 1 H), 6.82 (dt, *J* = 1.2, 7.9 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.6, 21.6, 22.2, 32.8, 34.2, 37.2, 38.8, 41.3, 44.2, 52.5, 52.6, 55.3, 59.1, 62.8, 109.5, 110.0, 115.7, 121.1, 125.6, 126.0, 132.8, 135.5, 137.5, 146.6, 172.1; HRMS calcd for $C_{27}H_{39}NO_6$: 473.2771. Found *m/z* (relative intensity) 474 (M^++1, 29), 473.2771 (M^+, 100), 472 (8), 442 (29), 400 (10).

4,4-Dimethoxycarbonyl-2-[4-(*p*-toluidino)-8-hydroxy-(1*E*)-octenyl]-1-isopropylidenecyclopentane (7t): IR (neat) 3395 (s), 2932 (s), 2862 (s), 1736 (s), 1520 (s), 810 (s) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.36-1.56 (m, 6 H), 1.57 (s, 3 H), 1.65 (s, 3 H), 2.05 (dd, *J* = 6.1, 13.2 Hz, 1 H), 2.20 (t, *J* = 5.9 Hz, 2 H), 2.21 (s, 3 H), 2.57 (dd, *J* = 8.4, 13.2 Hz, 1 H), 2.90 (br s, 2 H), 3.32 (m, 2 H), 3.62 (t, *J* = 6.3 Hz, 2 H), 3.69 (s, 3 H), 3.70 (s, 3 H), 5.29 (dd, *J* = 6.1, 15.1 Hz, 1 H), 5.36 (dt, *J* = 15.1, 5.9 Hz, 1 H), 6.49 (d, *J* = 8.2 Hz, 2 H), 6.95 (d, *J* = 8.2 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.3, 20.8, 21.6, 22.2, 32.7, 34.0, 36.9, 38.7, 41.2, 44.2, 52.6, 53.1, 59.1, 62.7, 113.4, 125.3, 125.9, 126.1, 129.6, 132.9, 135.7, 145.2, 172.1, 172.2; HRMS calcd for $C_{27}H_{39}NO_5$: 457.2828. Found *m/z* (relative intensity) 458 (M^++1, 35), 457.2834 (M^+, 100), 456 (11), 426 (28), 398 (4).

4,4-Dimethoxycarbonyl-2-[4-(*p*-chlorophenylamino)-8-hydroxy-(1*E*)-octenyl]-1-isopropylidenecyclopentane (7u): IR (neat) 3395 (s), 2932 (s), 1728 (s), 1567 (s), 1497 (s), 1435 (s), 1265 (s), 1065 (s), 818 (s), 732 (s) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.34-1.60 (m, 6 H), 1.56 (s, 3 H), 2.06 (dd, *J* = 5.6, 13.2 Hz, 1 H), 2.18 (m, 2 H), 2.55 (dd, *J* = 8.3 Hz, 13.2 Hz, 1 H), 2.90 (br s, 2 H), 3.30 (m, 2 H), 3.60 (t, *J* = 6.5 Hz, 2 H), 3.69 (s, 3 H), 3.70 (s, 3 H), 5.31 (m, 2 H), 6.47 (d, *J* = 8.8 Hz, 2 H), 7.06 (d, *J* = 8.8 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 15.2, 20.8, 21.5, 22.3, 32.6, 34.0, 36.9, 38.6, 41.1, 44.1, 52.6, 52.9, 59.1, 62.5, 65.7,

114.1, 121.1, 125.0, 125.9, 128.9, 132.8, 135.8, 146.3, 172.1, 172.2; HRMS calcd for $C_{26}H_{36}ClNO_5$: 477.2282. Found *m/z* (relative intensity) 480 (M^++3, 10), 479 (M^++2, 39), 478 (M^++1, 31), 477.2277 (M^+, 100).

4,4-Dimethoxycarbonyl-2-[4-(*p*-methoxycarbonylphenylamino)-8-hydroxy-(1*E*)-octenyl]-1-isopropylidenecyclopentane (7v): IR (neat) 3387 (s), 2955 (s), 1736 (m), 1605 (m), 1528 (m), 1435 (m), 1258 (m), 802 (s) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.35-1.62 (m, 6 H), 1.55 (s, 3 H), 1.56 (s, 3 H), 1.65 (s, 3 H), 2.06 (dd, *J* = 5.7, 13.2 Hz, 1 H), 2.23 (m, 2 H), 2.54 (dd, *J* = 8.5, 13.2 Hz, 1 H), 2.90 (br s, 2 H), 3.30 (m, 3 H), 3.46 (m, 1 H), 3.63 (t, *J* = 6.3 Hz, 2 H), 3.69 (s, 3 H), 3.71 (s, 3 H), 3.84 (s, 3 H), 5.32 (m, 2 H), 6.51 (d, *J* = 8.9 Hz, 2 H), 7.82 (d, *J* = 8.9 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.8, 21.5, 22.3, 32.6, 34.1, 37.0, 38.6, 41.0, 44.1, 51.4, 52.3, 52.6, 52.7, 59.1, 62.6, 111.6, 117.8, 124.6, 126.0, 131.5, 132.8, 136.1, 151.4, 167.1, 172.1, 172.2; HRMS calcd for $C_{28}H_{39}NO_7$: 501.2727. Found *m/z* (relative intensity) 502 (M^++1, 16), 501.2729 (M^+, 48), 500 (5), 470 (100).

4,4-Dimethoxycarbonyl-2-[4-(*p*-cyanophenylamino)-8-hydroxy-(1*E*)-octenyl]-1-isopropylidenecyclopentane (7w): IR (neat) 3387 (br), 2924 (s), 1736 (s), 1605 (m), 1520 (m), 826 (m) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.36-1.61 (m, 6 H), 1.54 (s, 3 H), 1.65 (s, 3 H), 2.06 (dd, *J* = 5.6, 13.2 Hz, 1 H), 2.20 (dt, *J* = 13.9, 5.4 Hz, 1 H), 2.25 (dt, *J* = 13.9, 5.7 Hz, 1 H), 2.52 (dd, *J* = 8.5, 13.2 Hz, 1 H), 2.90 (br s, 2 H), 3.31 (m, 1 H), 3.43 (m, 1 H), 3.63 (t, *J* = 6.2 Hz, 2 H), 3.69 (s, 3 H), 3.71 (s, 3 H), 4.19 (br, 1 H), 5.29 (dd, *J* = 6.0, 15.3 Hz, 1 H), 5.33 (dt, *J* = 15.3, 5.7 Hz, 1 H), 6.52 (d, *J* = 8.9 Hz, 2 H), 7.37 (d, *J* = 8.9 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.8, 21.5, 22.3, 32.5, 34.0, 36.9, 38.6, 41.0, 44.1, 52.3, 52.7, 59.1, 62.5, 97.9, 112.3, 120.4, 124.4, 126.0, 132.7, 133.6, 136.3, 150.9, 172.1, 172.3; HRMS calcd for $C_{27}H_{36}N_2O_5$: 468.2624. Found *m/z* (relative intensity) 469 (M^++1, 31), 468.2616 (M^+, 100), 467 (4), 437 (33).

4,4-Dimethoxycarbonyl-2-[4-benzylamino-8-hydroxy-(1*E*)-octenyl]-1-isopropylidenecyclopentane (7x): (a mixture of 2 isomers in 1 : 1 ratio): IR (neat) 3408 (s), 2951 (s), 1732 (s), 1583 (w), 1435 (m), 1267 (s), 1074 (m), 735 (m) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, a major isomer was assigned) δ 1.30-1.92 (m, 6 H), 1.50 (s, 3 H), 1.63 (s, 3 H), 2.06 (dd, *J* = 5.9, 13.4 Hz, 1 H), 2.41 (dd, *J* = 7.6, 13.2 Hz, 1 H), 2.47 (dd, *J* = 7.6, 13.2 Hz, 1 H), 2.55 (dd, *J* = 8.4 Hz, 13.4 Hz, 1 H), 2.88 (br s, 2 H), 3.33 (m, 1 H), 3.61 (m, 2 H), 3.68 (s, 3 H), 3.69 (m, 1 H), 3.70 (s, 3 H), 4.44 (d, *J* = 12.7 Hz, 1 H), 4.35 (d, *J* = 12.7 Hz, 1 H), 5.15 (m, 1 H), 5.47 (dd, *J* = 7.1, 15.4 Hz, 1 H), 7.27 (m, 1 H), 7.39 (m, 2 H), 7.55 (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$, a major isomer was assigned) δ 20.9, 21.0, 21.6, 22.0, 29.9, 30.8, 33.3, 38.5, 40.8, 43.9, 48.4, 48.7, 52.7, 56.8, 59.1, 66.8, 122.0, 128.8, 129.2, 130.2, 132.4, 138.6, 172.0, 172.4; ^{13}C NMR (100 MHz, $CDCl_3$, a minor isomer was assigned) δ 19.8, 21.1, 22.0, 30.0, 31.4, 33.7, 38.6, 40.7, 43.9, 48.4, 48.6, 52.9, 56.5, 61.5, 62.6, 122.3, 126.4, 129.5, 129.6, 130.0, 132.3, 139.2, 172.0, 172.4; HRMS calcd for $C_{27}H_{39}NO_5$-OH: 440.2801. Found *m/z* (relative intensity) 440.2769 (M^+-OH, 100), 426 (M^+-OCH_3, 47).

4,4-Dimethoxycarbonyl-2-[4-(*p*-anisidyl)-8-hydroxy-(1*E*)-octenyl]-(1*Z*)-1-(2-butylidene)cyclopentane (8): IR (neat) 3395 (s), 2862 (s), 1736 (m), 1512 (m), 1443 (m), 1242 (m), 1042 (w), 972 (w), 817 (w) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.88 (t, *J* = 7.3 Hz, 3 H), 1.37-1.60 (m, 6 H), 1.62 (s, 3 H), 1.96 (dq, *J* = 4.6, 7.3 Hz, 2 H), 2.06 (dd, *J* = 5.9, 12.9 Hz, 1 H), 2.20 (br s, 2 H), 2.55 (dd, *J* = 8.4, 12.9 Hz, 1 H), 2.86 (br d, *J* = 16.6 Hz, 1 H), 2.92 (br d, *J* = 16.6 Hz, 1 H), 3.25 (m, 1 H), 3.32 (m, 1 H), 3.62 (t, *J* = 6.2 Hz, 2 H), 3.69 (s, 3 H), 3.70 (s, 3 H), 5.34 (m, 2 H), 6.59 (m, 2 H), 6.75 (d, *J* = 8.8 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 12.5, 18.4, 22.2, 27.3, 32.7, 33.9, 34.3, 36.8, 41.2, 43.8, 52.7, 55.8, 57.4, 62.6, 114.9, 115.2, 123.7, 132.4, 136.1, 141.1, 172.1, 172.2; HRMS calcd for $C_{28}H_{41}NO_6$: 487.2934. Found *m/z* (relative intensity) 488 (M^++1, 30), 487.2918 (M^+, 100), 442 (6), 428 (60).

(8*E*)-11,11-Dimethoxycarbonyl-5-(*p*-anisidyl)-8-pentadecene-13-yn-1-ol (9): ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.37-1.60 (m, 8 H), 1.75 (t, *J* = 2.8 Hz, 3 H), 2.06 (dt, *J* = 7.3, 5.9 Hz, 2 H), 2.70 (d, *J* = 2.8 Hz, 2 H), 2.71 (d, *J* = 6.8 Hz, 2 H), 3.25 (m, 1 H), 3.62 (t, *J* = 6.2 Hz, 2 H), 3.69 (s, 3 H), 3.70 (s, 6 H), 5.21 (dt, *J* = 15.4, 7.6 Hz, 1 H), 5.53 (dt, *J* = 15.4, 6.8 Hz, 1 H), 6.59 (m, 2 H), 6.75 (d, *J* = 8.8 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 3.5, 22.0, 23.0, 29.0, 32.7, 35.4, 38.6, 52.5, 52.6, 55.8, 59.0, 62.6, 73.3, 78.8, 114.9, 125.2, 131.6, 134.9, 152.1, 170.4; HRMS cald for $C_{26}H_{37}NO_6$: 459.2621. Found *m/z* (relative intensity) 460 (M^++1, 29), 459.2610 (M^+, 100).

4,4-Dimethoxycarbonyl-2-[4-(*p*-anisidyl)-8-hydroxy-(1*E*)-octenyl]-(1*Z*)-1-(1-trimethylsilyl-2-propyliene)cyclopentane (10): IR (neat) 3364 (m), 2947 (s), 1728 (s), 1512 (s), 1458 (m), 1296 (s), 1242 (s), 1180 (s), 1042 (s), 972 (w), 849 (s), 756 (w), 694 (w) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.09 (s, 9 H), 1.28 (d, *J* = 13.4 Hz, 1 H), 1.45-1.70 (m, 6 H), 1.66 (s, 3 H), 1.86 (d, *J* = 13.4 Hz, 1 H), 1.96 (dd, *J* = 7.0, 13.1 Hz, 1 H), 2.23 (m, 2 H), 2.62 (ddd, *J* = 1.2, 8.4, 13.1 Hz, 1 H), 2.87 (br d, *J* = 15.9 Hz, 1 H), 2.98 (br d, *J* = 15.9 Hz, 1 H), 3.21 (m, 1 H), 3.31 (m, 1 H), 3.66 (t, *J* = 6.3 Hz, 2 H), 3.76 (s, 3 H), 3.80 (s, 3 H), 3.81 (s, 3 H), 5.30 (dd, *J* = 7.5, 15.3 Hz, 1 H), 5.38 (dt, *J* = 6.6, 15.3 Hz, 1 H), 6.58 (d, *J* = 8.8 Hz, 2 H), 6.78 (d, *J* = 8.8 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 2.6, 25.3, 28.2, 35.8, 37.0, 39.7, 42.2, 44.7, 47.6, 58.9, 61.8, 61.9, 62.5, 65.8, 118.0, 118.1, 128.2, 131.1, 133.3, 139.5, 155.0, 175.3, 175.6; HRMS calcd for $C_{30}H_{47}NO_6Si$: 545.3173. Found *m/z* (relative intensity) 546 (M^++1, 37), 545.3171 (M^+, 100), 544 (10).

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[10] Crystallographic data of **2g** and **11** have been deposited with the Cambridge Crystallographic Data Center as supplementary publication number CCDC-209610 and CCDC-634945. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, U.K. (fax: (+41)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

公表論文

第 1 章

Nickel catalyzed Grob fragmentation: ω-dienyl aldehydes synthesis

Masahiko Mori, Masanari Kimura, Yushi Takahashi and Yoshinao Tamaru

Chem. Commun., **2006**, 4303-4305.

第 3 章

Nickel-Catalyzed Addition of Dimethylzinc to Aldehydes across Alkynes and 1,3-Butadiene: An Efficient Four-Component Connection Reaction

Masanari Kimura, Akihiro Ezoe, Masahiko Mori, and Yoshinao Tamaru

J. Am. Chem. Soc. **2005**, *127*, 201-209.

第 4 章

Nickel catalyzed stereoselective conjugate addition of dimethylzinc upon aldimines across 1,3-dien-8-ynes and 1,3-dien-9-ynes

Masanari Kimura, Masahiko Mori , Nahoko Mukai, Keisuke Kojima and Yoshinao Tamaru

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Remarkably High 1,5-Diastereoselectivity in a Nickel-Catalyzed Conjugate Addition of Me_2Zn and Carbonyl Compounds to 1,ω-Dienynes with Through-Space Couplilng

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Regio- and Stereoselective Nickel-Catalyzed Homoallylation of Aldehyes with 1,3-Dienes

J. Am. Chem. Soc. **2006**, *128*, 8559-8568.

Masanari Kimura, Akihiro Ezoe, Masahiko Mori, Keisuke Iwata, and Yoshinao Tamaru

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